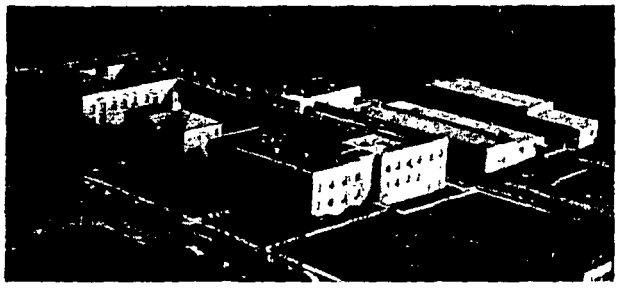

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

RESEARCH ON SMELT-WATER REACTIONS

Report Five

to

Advisory Technical Committee

1. Fifth Activity Report of Project Co-ordinator, IPC Project 2419.
2. Progress Report of The Babcock & Wilcox Company to March 5, 1965.
3. Progress Report of Combustion Engineering, Inc. to March 5, 1965.

March 26, 1965

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

FIFTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

Project 2419

March 26, 1965

In view of the tentative nature of research results and the early stage of the research here reported, readers are cautioned against drawing premature conclusions and are advised to await definite recommendations which will be offered when the significance of the technical work has been confirmed and conclusions become warranted.

Distribution:

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The Babcock & Wilcox Company - Messrs. Darmstadt, Markant (3), Moran
Combustion Engineering, Inc. - Messrs. Hochmuth, Lawler, Nelson (2), Ulmer
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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

FIFTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

This report covers activities of the Project Co-ordinator from November 15, 1964 to March 26, 1965. Work by the research organizations of The Babcock & Wilcox Company and of Combustion Engineering, Inc. is presented in attached reports, covering the period from November 6 through March 5. The Project Co-ordinator visited the CE Kreisinger Development Laboratory on January 7, the B&W Research Center on January 14, and met with the B&W research group in Cleveland, Ohio, on February 5.

Work on the chemical aspects of smelt-water explosions by Babcock & Wilcox has developed further fundamental information regarding the possibility of generating explosive gases within recovery furnaces. The production of combustible gases by several mechanisms from smelt-water-char-black liquor systems has been amply demonstrated in this program and in previous work. The problem now is to determine whether or not the gases are generated in sufficient quantity, and in the presence of an ignition source and sufficient oxygen, so that a gaseous explosion results. The B&W program will also explore the possibility of explosions resulting from water and the presence of elemental sodium in the smelt or char bed.

Study of the physical aspects of smelt-water explosions is making encouraging progress at Combustion Engineering. The use of high-speed motion pictures and the measurement of pressure waves is helping to characterize these explosions in more definite terms. Refinements are being made in the technique

of producing small-scale laboratory explosions. The effort to develop an additive which would render smelt nonexplosive by preventing the encapsulation of water has sufficient promise to justify the current major emphasis in this direction.

The Project Co-ordinator has continued to explore possible sources of specialized experience which might contribute to this research project. On December 3, a meeting in Appleton was held with Dr. A. I. Andrews of the School of Ceramics, University of Illinois, an expert in the field of ceramic enamels. Dr. Andrews felt that we were approaching our smelt additive research problem on a reasonable basis, that we would have to solve the problem experimentally, and that there was little in the way of previous ceramic research or experience that might be useful to us.

On December 7, the Project Co-ordinator visited Professor Lawrence H. Van Vlack, Department of Chemical and Metallurgical Engineering, University of Michigan. He is a recognized leader in the new field of solid state science. He pointed out that most of the fundamental work in solid state science has been done on simple systems. Our research is dealing with such a complex system that an experimental, rather than a theoretical, approach is likely to be most helpful.

A visit was made on January 5 to Dr. Norbert J. Kreidl, School of Ceramics, Rutgers University. Formerly Director of Materials Research for Bausch & Lomb Optical Company, he confirmed that the viscous nature of glass melts probably prevents the firm encapsulation of water under conditions similar to those which cause explosions when water is in contact with kraft smelts.

On January 7, a conference was held at CE's Kreisinger Development Laboratory with Dr. A. R. C. Westwood, Associate Director of the Research Institute for Advanced Studies, Baltimore, Maryland. B&W was represented at this

meeting by Dr. F. O. Ekman. The discussion was directed primarily toward the development of an additive to modify the explosive nature of smelt by weakening any encapsulating shell which might be formed by the addition of water. Dr. Westwood made a number of suggestions on experimental techniques, and proposed several ways of altering the crystalline structure and strength of solidified smelt. We believe that Dr. Westwood may prove to be an effective consultant to this phase of our program.

On January 8, the Project Co-ordinator met in Boston with Dr. F. H. Norton, formerly Professor of Ceramics at M.I.T. and now consulting in affiliation with Arthur D. Little, Inc. He felt that we were conducting a sound program, offered a suggestion for a smelt additive, but did not feel that he was in a position to contribute significantly to our project.

Also on January 8, a general discussion of the research program was held with Professor Glenn C. Williams, Department of Chemical Engineering, M.I.T. He has had a long experience in combustion, explosion, and exotic fuel research and has agreed to serve as a consultant in the areas of combustion and explosion technology. On January 25, Dr. Williams and the Project Co-ordinator visited the Westbrook, Maine mill of S. D. Warren Company, in order to familiarize Dr. Williams with the normal operating conditions of black liquor recovery furnaces.

On January 9, the Project Co-ordinator visited Professor Woldemar A. Weyl, School of Mineral Industries, Pennsylvania State University, who is an expert in the materials science field. Dr. Weyl was particularly interested in the possibility of elemental sodium contributing to smelt-water explosions, and regarded as reasonable the hypothesis of physical explosions caused by the encapsulation of water in a shell of solidified smelt.

The visit to State College, Pennsylvania, afforded an opportunity for the Project Co-ordinator to talk with Dr. Erik Rosén, who has come from Sweden for a year of postdoctoral research on solid state reactions. From our conversation, it appeared that our program on the chemical aspects of smelt-water explosions at B&W is well informed on the full scope of Dr. Rosén's previous research on recovery furnace reactions, and that Dr. Rosén is not aware of any current research in Scandinavia that might bear on our problem.

On March 25, Dr. Rosén visited, under other auspices than this project, The Institute of Paper Chemistry. His visit afforded a further opportunity for the Project Co-ordinator to discuss with him the general features of this research program.

An effort is being made to establish a consulting relationship with the Explosives Research Center of the U. S. Bureau of Mines at Pittsburgh, Pennsylvania. This group has an extensive background in combustion, ignition, and explosion technology. Since a continuing consulting arrangement is contemplated, a formal contractural arrangement is necessary, and we are presently engaged in negotiating a mutually satisfactory agreement. It is anticipated that the Explosives Research Center will be particularly helpful in the observation of plant conditions following an explosion in order to better identify the explosion mechanism responsible for the incident.

It has been recognized that structural analysis of the damage pattern from recovery furnace explosions may also be effective in determining the explosion mechanism. This is a highly specialized field, and there are only a few people who are qualified to undertake work of this type. The possibility of consulting services for damage analysis had been discussed with Professor Robert J. Hansen, Civil Engineering Department, M.I.T., who has an outstanding reputation

in this field. A proposal for such work has been received from the Structural Mechanics Section of the Solid Mechanics Research Division of the Illinois Institute of Technology Research Institute. Further discussions will be needed before a definite relationship is established.

The Project Co-ordinator attended the annual meeting of the Technical Section of the Canadian Pulp and Paper Association, held in Montreal, January 26-29. The meeting provided an opportunity to talk with a number of people in the Canadian industry about experiences relating to recovery furnace safety and to attend a session of papers relating to safe operation of recovery furnaces. Liaison has been maintained with the Subcommittee on Emergency Shutdown Procedures of the Black Liquor Recovery Boiler Advisory Committee.

A visit was made on January 15 and 16 to the mill of Allied Paper Corporation, Jackson, Alabama, to observe conditions resulting from an explosion on January 12. The Project Co-ordinator was accompanied by Wharton Nelson of Combustion Engineering, Inc. and by Joseph M. Kuchta of the Explosives Research Center of the Bureau of Mines. Furnace damage was light, and operations were restored in four days. There were no injuries involved. It appeared that the explosion was caused by combustible gas, with no indication of a smelt-water reaction. It could not be determined whether the explosion was caused by gases from the pyrolysis of black liquor which had been used to quench a corner of the char bed at which a bottom leak of smelt had developed, or whether the explosion resulted from unburned gas that had accumulated in the furnace during an attempt to light auxiliary gas burners. The full co-operation of the Allied management with our observation of the circumstances of the explosion is greatly appreciated.

On March 19 through March 23, the Project Co-ordinator visited the mill of Southwest Forest Industries, Snowflake, Arizona. A fully ruptured primary

superheater tube had led to a recovery furnace explosion on March 18. Fortunately, there were no injuries. Principal damage was a major opening almost the full height of the left front corner of the furnace, with varying deflection of buckstays on the front and left sides. Repairs will probably require about four weeks. Our observations were augmented by the presence, on an emergency basis, of two consultants to the research program. These were Joseph M. Kuchta, Explosives Research Center, Bureau of Mines, and Richard R. Robinson, Research Engineer, Structures Research, Illinois Institute of Technology Research Institute. At the present time, our considerations of the probable mechanism of this explosion have been unable to conclusively distinguish between the possibilities of a combustible gas explosion or a physical explosion from smelt-water reaction. We hope that further study may enable a definite determination of the explosion mechanism. The full co-operation of the Southwest organization has been of great assistance.

In summary, research on the chemical aspects of smelt-water explosions indicates that combustible gases are evolved from some reactions of smelt with water and also from the pyrolysis of black liquor if used to "black out" a char bed during an emergency. To prevent explosions from these sources we already have available or should be able to develop techniques for safe operation, such as inerting or purging furnace atmospheres, use of pilot burners, or elimination of the "blacking out" procedure. The concept of physical explosions caused by the encapsulation of water in a shell of solidified smelt appears to be a useful working hypothesis, not yet proved, but consistent with the known experimental facts. The development of an additive which would prevent physical smelt-water explosions by weakening or preventing encapsulation is a promising approach, although we are working here in a field where there is little fundamental or theoretical information available to guide us. Ultimate success in this research

project cannot be predicted with certainty but results to date justify our effort to understand better the mechanisms of smelt-water explosions.

THE INSTITUTE OF PAPER CHEMISTRY

Howard S. Gardner

Howard S. Gardner
Co-ordinator, Smelt-Water Research Project
Senior Research Associate
Administrative Staff

PROGRESS REPORT

FOR THE PERIOD OF NOVEMBER 6, 1964 TO MARCH 5, 1965

TO

H. S. GARDNER, PROJECT COORDINATOR,
THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

THE BABCOCK & WILCOX COMPANY
RESEARCH CENTER
ALLIANCE, OHIO

April 1, 1965

PROGRESS REPORT OF THE BABCOCK & WILCOX COMPANY
ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between November 6, 1964 and March 5, 1965 and the present status of this project. As outlined in our previous reports, our over-all objective is to determine which chemical reactions occur between the smelt-char-combustion gas system that result in explosive reactions with water. A further objective is to determine the thermal decomposition products of black liquor. Having determined these reactions and reactive products, a basis for preventive measures and procedures can be formulated.

SUMMARY OF WORK

During this report period the following work was accomplished:

1. A large number of possible individual reactions of smelt with water have been examined from a theoretical standpoint. Although most are endothermic, several exothermic reactions could take place and cannot be ruled out at this time as possible causes of explosions.
2. The computer programing, allowing a comprehensive calculation of reaction products, has been completed (assuming condensed phases at unit activity) and the computer time for one problem has been reduced to 5 minutes/run.
3. The equilibrium reaction products for eight different smelt compositions with water at three levels of concentration have been calculated. These results show that small amounts of carbon and sodium sulfate in the sodium sulfide-carbonate smelt result in a large increase in potentially explosive constituents. In general, the lower the ratio of water to smelt, the higher the proportion of explosive gases.

4. The equilibrium products of the combustion of black liquor solids from 0-120% total air have been calculated. These calculations show that sodium vapor can form at temperatures above 1700°F.
5. The volumes of gas resulting from black liquor solids decomposition were obtained experimentally as a function of temperature between 600°F and 1800°F.
6. Gas samples taken at each temperature during the black liquor solids decomposition were analyzed. The analysis shows that large amounts of potentially explosive gas are formed.
7. Laboratory tests of the reaction of Na_2S with water vapor showed relatively high yields of hydrogen and hydrogen sulfide.
8. Laboratory studies aimed at determining the equilibrium constant of

   $1/4\ Na_2S + H_2O = 1/4\ Na_2SO_4 + H_2$

   were carried out by the reverse reaction. The results are in reasonable agreement, in the temperature range studied, with Rosen's calculations. However, our data show the reaction to be slightly exothermic, (-2000 cal.) and this is more than other investigators have indicated.
9. Work has been initiated toward an experimental method for determining if elemental sodium can exist in smelt.
10. Design work is 90% completed for the pressure vessel assembly which will be used to study smelt-liquid water reactions. A bench-scale autoclave is on order from Autoclave Engineers, Inc. and delivery is expected March 22.

STATUS

Chemical Equilibrium Studies

Theoretical studies of the chemical equilibria involved in the Kraft recovery

process and smelt-water reactions are being made in order to provide an insight to the chemical reactions which are taking place and to provide guidelines to our experimental work. Two approaches have been used, (1) the consideration of individual reactions of smelt-char-gaseous products with water, and (2) a comprehensive calculation, by computer techniques, of the over-all equilibrium concentrations of individual products expected to exist when the specified reactants are brought together. The first approach is useful as a very rough guideline to the possible reactions, while the second can be used for more quantitative estimations.

A summary of the individual reactions studied to date is presented in Figures 1-3 in which the log of the equilibrium constant is plotted as a function of temperature. The ΔH at 1200°K (1700°F) of the individual reaction is also indicated.

Some caution should be exercised in the interpretation of these reactions as written. First of all, it must be kept in mind that a reaction will proceed, in spite of an unfavorable equilibrium relationship, if one or more products are continuously removed from the reaction, e.g., the formation of gaseous products. Furthermore, if one of the products is initially absent, the reaction will proceed until the concentrations of the products meet the equilibrium criterion. It has been pointed out in previous reports that the thermodynamic properties of Na_2S are not well established; except for Na_2SO_3, the properties of most of the other compounds are reasonably reliable. In the equations presented in Figures 1-3 the data of Rosen[1] was used for all reactions.

Equations 1-13 represent the reactions which might be expected from smelt constituents and water. All are written in relation to one mole of water in order to interpret the results on the same basis. Reactions 1-4 were previously discussed in our September 1, 1964 progress report. It was pointed out at that time that the reaction represented by equation (4),

$$Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S$$

was an exothermic reaction, but that the equilibrium constant became favorable only at lower temperatures (≈1200°F). Equation (11) also illustrates an exothermic reaction with a more favorable equilibrium constant which would take place in a reducing atmosphere, such as would exist in the smelt bed.

$$1/2\ Na_2S + 1/2\ CO + H_2O = 1/2\ Na_2CO_3 + 1/2\ H_2S + 1/2\ H_2$$

Equation (9), showing the reaction of water with COS, is also an exothermic reaction with a slightly more favorable equilibrium constant. COS would be expected to be a minor constituent of the char bed-smelt atmosphere, as could be inferred from reactions 16-18 shown in Figure 3.

Reactions giving rise to elemental sodium are illustrated in equations 14, 15 and 16. As noted previously, these would be expected to take place at temperatures above 1700°F.

Although the individual reactions listed above are a rough guideline to the mechanism of smelt-water reactions, an over-all calculation of product yields expected from specified reactants is much more meaningful because it takes into account all of the chemical reactions and interactions and furthermore can take into account the laws of mass action. As indicated in previous reports, we have been programing our computer to calculate the equilibrium concentrations of compounds, both gaseous and condensed, which would be expected to be present at equilibrium when specified reactants are brought to equilibrium.

This programing work has now been completed and the method is broad enough to allow a consideration, not only of smelt-water reactions, but also of black liquor combustion and pyrolysis products under a wide variety of conditions. The results of these studies are discussed below and should be viewed in light of the following limitations of the method:

(1) The method assumes complete equilibrium between reactants and products.

(2) While the thermodynamic data are reasonably good for most species, the fundamental data for Na_2S has the greatest uncertainty, (our experimental work, described further in the report will serve to reduce such uncertainty to acceptable proportions).

(3) The method, as it now is used, assumes unit activity for all condensed species. This can cause serious errors in the calculation of the smelt-water reactions but should not affect the combustion calculations to any marked degree. The extent and the direction of this error in the smelt-water reactions can be estimated.

Smelt-Water-Char Reactions - In order to obtain an indication of the relative effects of the components of smelt and char, as well as the effect of variable amounts of water, the following smelt compositions were used as reactants, with water at a ratio of 10 lbs, 1 lb, and 0.1 lb of water per 100 lbs of smelt-water mixture.

1. 25% Na_2S, 75% Na_2CO_3
2. 35% NaS, 65% Na_2CO_3
3. 24.75% Na_2S, 74.25% Na_2CO_3, 1% carbon
4. 22.5% Na_2S, 72.5% Na_2CO_3, 5% carbon
5. 24.75% Na_2S, 74.25% Na_2CO_3, 1% Na_2SO_4
6. 22.5% Na_2S, 72.5% Na_2CO_3, 5% Na_2SO_4
7. 24.66% Na_2S, 73.99% Na_2CO_3, 1.0% Na_2SO_4, 0.338% C
8. 24.41% Na_2S, 73.24% Na_2CO_3, 1.0% Na_2SO_4, 1.338% C

The equilibrium calculations were carried out at 100°K increments between 800°K-1600°K (981°F-2421°F).

Although all of the results will not be given in this report, illustrative examples of the results obtained for the case (7) and (8) above are shown in Tables I-VI.

As generalities, these calculations have shown the following:

1. The lower the water/smelt ratio, the higher the percent of explosive gas formed. This might explain situations where large amounts of water have entered the smelt bed with no explosion taking place, and further, would indicate that the most dangerous conditions would arise if a large surface area of smelt were exposed to a water spray. Thus the physical character of a leak in a boiler pressure part could be significant.
2. The effect of higher sulfidity was largely one of giving increased amounts of H_2S.
3. Carbon additions to smelt and particularly carbon in the presence of sodium sulfate, gave the highest amounts of potentially explosive gas as well as the highest total volume of gas. This can be interpreted partially as an effect of the water-gas reaction. In the presence of a molten smelt it would not be expected that the water-gas reaction would be self-quenching because of the latent heat content of the smelt. Furthermore, it is significant that relatively small amounts of carbon can contribute substantially to the formation of H_2, H_2S, and CO.
4. The calculations confirm that at lower temperatures the reaction discussed previously,

   $$Na_2S + H_2O + CO_2 = Na_2CO_3 + H_2S$$

   takes place with the generation of H_2S.
5. Sodium hydroxide gas is formed in almost every case at temperatures of 1700°F and above. The significance of this gas is not now apparent except as it contributes to the over-all gas volume generated.

Black Liquor Combustion - In order to determine the conditions which would be expected to exist in the different zones of the furnace, it is planned to carry out equilibrium calculations of products expected under the conditions of variable fuel,

a wide range of total air and a range of temperatures. Such calculations will show conditions which may exist in the smelt bed, for example, and give clues concerning the existence of explosion precursors. Initial calculations have been carried out and have been completed for the case of the combustion of black liquor solids over a range of 0-120% total air and 900°K-1700°K (1161°F-2601°F).

The basis for the calculations is as follows:

1. Elemental Liquor Analysis:

Na	18.3%
C	42.6
H	3.6
S	3.6
O	31.7
Inert Oxides	0.2

2. Salt Cake Make-up = 4.17 lb/100 lb solids

3. Theoretical air gives smelt of following composition:

Na_2S	28.5%
Na_2SO_4	1.5
Na_2CO_3	70.0
	100.0

This basis is the same as outlined by Clement, Coulter, and Suda[2].

Illustrative results are shown in Tables 7-10 for 0, 30, 60 and 100% air. While a thorough discussion of these results will not be attempted in this report, several pertinent items should be noted. The results found at 0.0% air can be considered as a calculation of the theoretical products of decomposition of black liquor solids and show the large amounts of combustible and explosive gas that can be formed. The results at low total air also show that sodium vapor is formed at temperatures above 1701°F. If elemental sodium is soluble in the smelt,

small amounts could be present, but whether it exists in significant amounts is a question which will have to be resolved by experiment.

The exothermic reaction of COS with water, discussed previously, raised the question whether significant amounts of COS would be present. These calculations show that under these conditions, in general, only traces of this gas would be expected. When calculations have been completed of the black liquor solids less the volatile gas, a condition postulated to exist in the bed, more firm conclusions can be drawn concerning the significance of this gas.

It may be noted again in passing that sodium hydroxide is the predominant form of volatile sodium compounds, even at 30% total air.

EXPERIMENTAL

Black Liquor Decomposition Studies

In previous reports it has been pointed out gaseous explosions resulting from the release of volatile and explosive decomposition products of black liquor during an emergency shut-down are a distinct possibility. As a result, we have previously reported studies showing that black liquor decomposition is essentially an endothermic process and that the black liquor can be considered to decompose in a two-step process. The first step involves the evaporative loss of water and the second step involves the thermal decomposition of the organic solids. In order to further identify the importance of this latter step, experimental work was carried out in order to determine the amount and the composition of the gaseous products.

The moisture was removed from a strong black liquor, with salt cake addition, and known amounts of the black liquor solids were placed in the cool end of a tube furnace arrangement shown in Figure 4. The tube and the sample bottle were evacuated, the furnace brought to the desired temperature and the sample then pushed into the heated zone. The gas pressure produced was measured and the

volume corrected to standard conditions. Initial runs at low temperatures (600-800°) showed that a 10 minute residence time in the furnace resulted in release of at least 99% of the volatile material, and this time interval was used as standard. A plot of volume vs time at constant temperatures, is shown in Fig. 5.

The volume of gas, reduced to standard temperature and pressure, resulting from these decomposition studies is shown as a function of temperature in Fig. 6. The plot shows that relatively large volumes of gas result from modest (1200-1400°) temperatures.

Each sample of gas was analyzed for its individual constituents by gas chromatographic methods and the analysis of the gas at each temperature is shown in Table XI.

These results show the character of the gases evolved during thermal decomposition. It will be noted that the gas analysis is much different than calculated in Table VII because of the non-equilibrium conditions of the laboratory experiment. At the lower temperatures CO_2 and SO_2 are present in relatively large amounts. The percent of H_2S is greatest at lower temperatures, as might be expected. CO is present in large quantities and the H_2 content becomes significant above 1000°F. We have made rough estimations of the explosive limits of the gases. At 800°F the gas is explosive in air from 21% to 60%. At 1600° the limits are broader and in air it is estimated the gas would be explosive between 7.8% and 59%. It can readily be appreciated that during an emergency shut-down in which black liquor is used for black out that there are significant quantities of explosive gases and water vapor evolved. We are presently working on a more detailed consideration of the implications of the presence of such explosive gases during shut-down.

Na_2S - H_2O Reaction

It has been pointed out in previous reports and in this report that the fundamental thermodynamic properties of Na_2S are not known to a high degree of

certainty. As it appears that Na_2S is probably the most reactive chemical in smelt, it is of importance to determine by experiment what the reaction products with water are. Furthermore, if some of the fundamental thermodynamic properties of Na_2S could be determined at the same time, more confidence could be placed on our equilibrium calculations.

As an initial preliminary test the following experiment was carried out. Helium gas was equilibrated with water vapor and passed over anhydrous Na_2S at 1650°F at the rate of 0.5 liter/minute. The exit gas was analyzed for H_2 and H_2S at intervals until the concentration of each was constant. The test apparatus is illustrated in Figure 7, and the results of this experiment are shown graphically in Figure 8. Initially, exceptionally high hydrogen values (in relation to the water vapor present) were found and this amount gradually decreased to a constant value while the experiment was being carried out. H_2S was also found in unexpectedly high concentrations. Apparently two reactions took place,

$$1/2\ Na_2S + H_2O = NaOH + H_2S$$

$$1/4\ Na_2S + H_2O = 1/4\ Na_2SO_4 + H_2$$

Our interpretation of these results is that the initial high concentrations of H_2S and H_2 were due to the initial absence of NaOH and Na_2SO_4 and as a result the reaction was driven to the right. As more NaOH and Na_2SO_4 formed, equilibrium was ultimately achieved. However, the yield of each gaseous product (H_2 and H_2S) was greater than would have been predicted from a consideration of equilibrium constants alone (equations 3 and 5, Fig. 1). Thus it appears that these results indicate that solution effects took place to an unknown degree and illustrate the importance of these effects.

From a practical point of view, this experiment illustrated what could take place in a smelt initially containing neither sodium sulfate nor sodium hydroxide,

and demonstrated that significant quantities of hydrogen and hydrogen sulfide can be generated at 1650°F from the reaction of water with sodium sulfide.

From a theoretical point of view, no fundamental data were obtained because of the complicating factor of solution formation between Na_2SO_4, Na_2S, and NaOH.

Na_2SO_4 - H_2 Reaction

An alternate method of obtaining fundamental thermodynamic data (ΔS) for Na_2S is to carry out the reaction:

$$H_2 + 1/4\ Na_2SO_4 = H_2O + 1/4\ Na_2S$$

If the hydrogen concentration is kept at approximately 1%, the amount of water estimated to be formed should be insufficient to result in the formation of sodium hydroxide. Thus, solution effects can be eliminated, and the side reaction forming H_2S should be minimized. In order to eliminate solution effects between Na_2S and Na_2SO_4 the reaction must be carried out at temperatures below 1500°F. Although these temperatures are somewhat lower than are of immediate interest, all of the data available indicate that the reaction equilibrium is not affected markedly by temperature. Thus if the equilibrium constant can be determined at the lower temperatures, a relatively safe extrapolation can be made to the higher temperatures of interest.

This experiment was carried out in a tube furnace similar to Figure 7 with the following modifications. A platinum liner was placed inside the alundum tube and a mixture of sodium sulfate and fused zirconia globules placed inside the liner. The ends of the liner were capped with platinum screens in order to keep the charge intact. Argon containing 1.08% H_2 (by analysis) was passed through the furnace at flows from 500 cc/min down to 25 cc/min. The exit gas was analyzed by gas chromatography at intervals for hydrogen content and at the lowest flow rates the hydrogen content became constant. From these hydrogen values an equilibrium constant could

be calculated. The tests were carried out at 100°F intervals from 1100°F to 1400°F inclusive.

In order to ensure that hydrogen was not lost by diffusion through the apparatus, the 1.08% and 0.05% H_2 standard samples were passed through the entire system, less the sodium sulfate charge, at 1300°F at the same flows as used in the equilibrium experiment. No loss of hydrogen was detected.

Through these experiments the equilibrium constant for the reaction

$$1/4\ Na_2S + H_2O = 1/4\ Na_2SO_4 + H_2$$

has been determined and these results are compared below with those calculated from Rosen's[1], May's[3], and Bauer and Dorland's[4] data.

	Equilibrium Constant			
	Experimental	Calculated from Thermal Data		
	B&W	May	Rosen	Bauer and Dorland
981	-	.076	.038	.041
1100	.044			
1200	.041			
1300	.035			
1341	-	.074	.039	.039
1400	.034			

These results show that the measured equilibrium constant in the temperature range is in reasonable agreement with that calculated from Rosen's[1] and Bauer and Dorland's[4] data, but is considerably less than indicated from May's[3] thermal data. Because of the agreement with Rosen, we shall continue to use his data for our calculations.

The equilibrium constants tabulated above are the average of at least four determinations at each temperature. Furthermore, the hydrogen determinations at the exit of the reaction furnace were of high precision (better than ± .001%). Therefore we place reasonable confidence in these values and feel that the change

of the equilibrium constant with temperature that we observed is a real one.

Although the equilibrium constant as determined experimentally is in reasonable agreement with Rosen's, this change of equilibrium constant with temperature gives a significant slope, and is in contrast to all other calculations. Such dependence of the equilibrium constant on temperature is of significance because the slope of a plot of log K_{eq} against $\frac{1}{T}$ gives a measure of the ΔH of the reaction. Figure 9 shows such a plot over the temperature range of interest for May's, Rosen's and Bauer and Dorland's calculations as well as the B&W experimental data. Two plots are shown for May's data, one using his thermal data for both Na_2S and Na_2SO_4, the other using Coughlin's[5] data for Na_2SO_4 (and May's data for Na_2S). The significant point to be noted is that our data show, at the temperatures we investigated, that the reaction is exothermic, roughly 2,000 cal. On the other hand, calculations from thermal data show the reaction to be almost neutral, then becoming endothermic in character at higher temperatures.

If, indeed, this reaction is endothermic at high temperatures (1800°) and exothermic at a lower temperature (1400°), as our data indicate, this is a somewhat unusual reaction and leads to the conclusion that there must be some critical temperature where the reaction changes from exothermic to endothermic (as the temperature is raised). Although the magnitude of the ΔH is such that it is possible that this change of the character of the reaction may not be significant, nevertheless it is of interest to note that the Combustion Engineering experiments indicate that there is a critical temperature range (≈1550°F) at which the smelt-water reaction appears to take place with explosive violence. While a complete explanation of this phenomenon has not been advanced, perhaps this change to an exothermic reaction as the temperature is lowered plays some part in the over-all mechanism.

Because of the ΔH of the reaction that we have observed we find the entropy of Na_2S at 1000°K to be 59.98 cal/mol/degree, a somewhat higher value than others have calculated. Although it would be pertinent to this project to investigate this equilibrium further, time does not permit us to do so and no further experiments of this type are planned.

Elemental Sodium Formation in Smelt

The question of whether elemental sodium plays a role in the explosions which have occurred in recovery boilers (and dissolving tanks) has been considered for many years but very little experimental work has been carried out. The problem involves finding answers to the following questions:

(1) Is elemental sodium formed in the bed of the furnace?

(2) If elemental sodium forms, does it dissolve in the smelt and become relatively "fixed" in spite of its known volatility?

(3) If sodium is present, and dissolved in the smelt, is it there in sufficient amounts to cause explosions with water?

We have initiated preliminary experiments aimed at answering these questions. Our initial experiments, just started, involve heating smelt constituents and carbon in a specially constructed graphite boat in a quartz tube in a horizontal furnace in the absence of air. After a period of time at temperature the reaction boat will be quickly removed from the heated zone to a cold, water-cooled section of the quartz tube. The reaction boat, after cooling, will be quickly placed in an Erlenmeyer flask filled with nitrogen, stoppered and water added dropwise through a separatory furnace and the evolved gas analyzed. By this method any metallic sodium present will react with the water and form hydrogen.

Reaction of Liquid Water with Smelt

In order to determine the reactions of smelt with liquid water, with an

explosive hazard present, it is necessary to contain this reaction in a pressure vessel. We have on order from Autoclave Engineers a small bench scale autoclave (6 1/2" O.D. x 15") designed for 5000 psi @ 650°F (with provisions for heating smelt to 2000°F) and delivery is promised for March 22. The design work for the accessory equipment, i.e., heaters, pressure transducers, method of introducing water in controlled amounts, atmosphere control, etc., is approximately 90% complete.

FUTURE WORK PLANNED

It is planned to carry out the following program during the remainder of this contract:

1. A consideration of the implications of the release of explosive gas from (a) black liquor decomposition, (b) smelt-water reactions, and (c) the water-gas reaction.
2. Computer calculations of black liquor combustion simulating the conditions that would be expected to exist in the various portions of the bed and the furnace.
3. Continue our experiments aimed at determining whether elemental sodium plays a part in the explosion mechanism.
4. Experimental determination of the gases released and their explosive potential as a result of a reaction between molten smelt and liquid water. This investigation will also consider other possible explosion mechanisms.

During the next quarter items (1) and (2) will be completed, and work will be continued on items (3) and (4). The bench scale containment vessel with its associated pressure measurement and other accessories will have been assembled and tests initiated by the end of the next quarter.

EXPENDITURES

Expenditures to March 1, 1965 are as follows:

Labor plus overhead	$75,567
Material	10,848
Total	$86,415

A cost control chart showing actual and anticipated expenditures is attached.

CHA:vlr

Submitted by: C. H. Anderson
C. H. Anderson

Approved by: W. A. Keilbaugh
W. A. Keilbaugh

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(1) Rosen, Erik, Trans. Roy. Inst. Tech., Stockholm, No. 159 (1960).

(2) Clement, J. L., Coulter, J. H., and Suda, S., TAPPI, 46, No. 2, 153A (1963).

(3) May, M. N., TAPPI, 35, 511-517 (1952).

(4) Bauer, Thomas W. and Dorland, Rodger M., Can. J. Tech., 32, 91-101 (1954).

(5) Coughlin, James P., J.A.C.S., 77, 868-870 (1955).

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	.001	.016	.079	.187	.349	.735	1.698	3.628	6.213
CO2	.085	.563	1.666	2.617	3.324	4.907	8.388	14.283	20.242
H2	5.871	5.984	6.143	6.357	6.772	7.002	6.418	4.488	2.062
H2O	90.457	90.360	90.223	89.825	87.921	81.808	68.301	45.357	20.017
H2S	3.586	3.075	1.872	.845	.433	.311	.275	.170	.065
SO2	.000	.000	.000	.002	.007	.022	.078	.233	.566
SO	.000	.000	.000	.000	.000	.000	.001	.005	.017
NA	.000	.000	.000	.000	.002	.018	.113	.524	2.030
NAOH(G)	.000	.001	.016	.167	1.191	5.195	14.729	31.305	46.779
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
NA2CO3(C)	69.2362	68.9442	68.2418	67.5878	67.0287	65.6671	62.0801	53.2368	35.8340
NA2S(C)	21.0952	21.2930	21.7749	22.1794	22.2837	22.2218	22.0554	21.7491	20.9174
NA2SO4(C)	.0843	.1154	.1738	.2527	.3882	.5765	.8247	1.2278	2.1274
TOTAL	90.4157	90.3525	90.1904	90.0199	89.7007	88.4653	84.9602	76.2137	58.8788

TABLE I

EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na_2S - 24.66%
Na_2CO_3 - 73.99
Na_2SO_4 - 1.00
Carbon - 0.338

WATER ADDED: 10#/90# SMELT

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	2.060	6.850	9.241	11.110	12.662	14.006	15.238	16.052	14.940
CO2	4.265	12.658	18.311	20.108	19.809	19.176	19.090	20.734	24.722
H2	38.046	33.326	26.934	23.247	21.001	18.887	15.538	9.427	3.152
H2O	18.569	26.639	36.982	42.383	44.836	45.265	41.937	31.262	15.543
H2S	36.991	20.386	8.433	3.062	1.316	.673	.384	.170	.062
SO2	.000	.000	.000	.000	.000	.001	.003	.012	.091
COS	.069	.141	.096	.048	.026	.017	.013	.010	.010
NA	.000	.000	.000	.000	.002	.021	.149	.760	2.577
NAOH(G)	.000	.000	.002	.041	.349	1.955	7.648	21.571	38.893
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
C(S)	.0238	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
NA2CO3(C)	75.5960	74.7698	73.9603	73.5315	73.3689	73.2404	72.9333	72.0171	70.0997
NA2S(C)	23.2448	23.8532	24.4491	24.7637	24.8734	24.9143	24.9317	24.9435	24.9407
TOTAL	98.8646	98.6229	98.4094	98.2952	98.2423	98.1547	97.8650	96.9607	95.0404

TABLE II

EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na_2S - 24.66%
Na_2CO_3 - 73.99
Na_2SO_4 - 1.00
Carbon - 0.338

WATER ADDED: 1#/99# SMELT

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	6.616	27.244	60.174	72.086	72.514	72.673	71.612	66.650	56.133
CO2	44.008	42.207	20.911	11.135	10.685	10.273	10.191	11.492	15.823
H2	1.206	8.575	14.414	14.418	13.845	13.006	11.160	6.916	2.095
H2O	1.891	5.747	3.471	2.243	2.784	3.218	3.421	3.062	1.759
H2S	38.876	14.664	.904	.090	.044	.026	.017	.009	.004
COS	7.403	1.563	.124	.015	.008	.005	.004	.003	.004
NA2	.000	.000	.000	.000	.000	.000	.000	.003	.014
NA	.000	.000	.000	.000	.007	.087	.604	2.793	7.804
NAOH(G)	.000	.000	.001	.013	.113	.712	2.990	9.067	16.356
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
C(S)	.1658	.1309	.0397	.0000	.0000	.0000	.0000	.0000	.0000
NA2CO3(C)	74.6310	74.3117	74.0146	73.9858	73.9821	73.9693	73.9175	73.7425	73.3918
NA2S(C)	24.7085	24.9436	25.1624	25.1834	25.1848	25.1853	25.1855	25.1857	25.1858
TOTAL	99.5053	99.3862	99.2167	99.1692	99.1669	99.1546	99.1030	98.9282	98.5775

TABLE III

EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na_2S - 24.66%
Na_2CO_3 - 73.99
Na_2SO_4 - 1.00
Carbon - 0.338

WATER ADDED: 0.1#/99.9# SMELT

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	.104	.902	2.452	3.789	4.815	5.891	7.499	9.598	10.104
CO2	.719	3.837	7.954	9.724	9.910	10.091	11.454	15.305	21.275
H2	31.192	29.154	25.813	23.493	21.999	20.111	16.185	9.155	2.864
H2O	50.889	53.647	58.011	60.791	61.781	60.295	53.260	37.480	17.971
H2S	17.094	12.446	5.746	2.124	.907	.472	.293	.151	.061
SO2	.000	.000	.000	.000	.000	.001	.003	.017	.161
COS	.002	.013	.018	.011	.007	.005	.005	.005	.008
NA	.000	.000	.000	.000	.002	.025	.174	.796	2.463
NAOH(G)	.000	.000	.006	.071	.578	3.110	11.127	27.491	45.081
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
NA2CO3(C)	76.0686	73.6226	69.7112	67.3562	66.3587	65.1485	61.7471	52.3491	34.0491
NA2S(C)	15.0022	16.8033	19.6822	21.3998	22.0041	22.2194	22.2971	22.3456	22.2336
TOTAL	91.0708	90.4258	89.3933	88.7560	88.3628	87.3679	84.0442	74.6948	56.2827

TABLE IV

EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na_2S - 24.41%
Na_2CO_3 - 73.24
Na_2SO_4 - 1.00
Carbon - 1.338

WATER ADDED: 10#/90# SMELT

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	2.065	16.109	42.028	55.400	58.885	59.625	58.896	55.211	47.485
CO2	4.287	14.757	10.201	2.761	.668	.187	.435	2.115	6.847
H2	37.897	39.401	40.133	39.798	39.495	34.345	22.653	13.510	3.715
H2O	18.545	15.613	6.750	1.998	.611	.189	.360	1.328	1.596
H2S	37.136	13.929	.857	.020	.001	.000	.000	.001	.002
COS	.070	.191	.030	.000	.000	.000	.000	.000	.001
NA2	.000	.000	.000	.000	.000	.018	.092	.067	.064
NA	.000	.000	.000	.001	.119	4.347	12.835	13.817	16.589
NAH	.000	.000	.000	.000	.000	.012	.031	.028	.019
NAOH(G)	.000	.000	.002	.023	.222	1.278	4.697	13.924	23.683
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
C(S)	1.0145	.8885	.5833	.3983	.3411	.2457	.0000	.0000	.0000
NA2CO3(C)	74.8533	73.7192	72.6236	72.5156	72.4896	72.0402	70.4576	68.7526	65.5889
NA2S(C)	22.9956	23.8306	24.6373	24.7157	24.7177	24.7178	24.7178	24.7177	24.7172
TOTAL	98.8634	98.4384	97.8442	97.6296	97.5494	97.0037	95.1754	93.4703	90.3061

TABLE V

EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na_2S - 24.41%
Na_2CO_3 - 73.24
Na_2SO_4 - 1.00
Carbon - 1.338

WATER ADDED: 1#/99# SMELT

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	6.723	27.524	60.598	79.234	84.156	83.473	64.222	62.674	58.379
CO2	45.435	43.080	21.207	5.647	1.364	.367	.182	.966	3.761
H2	1.095	8.071	13.827	14.072	13.990	12.767	1.694	.716	.127
H2O	1.748	5.465	3.353	1.010	.309	.098	.010	.028	.024
H2S	37.107	14.232	.886	.020	.001	.000	.000	.000	.000
COS	7.891	1.628	.128	.004	.000	.000	.000	.000	.000
NA2	.000	.000	.000	.000	.000	.007	.573	.364	.261
NA	.000	.000	.000	.001	.070	2.624	32.068	32.230	33.487
NAH	.000	.000	.000	.000	.000	.004	.021	.015	.007
NAOH(G)	.000	.000	.001	.012	.110	.658	1.230	3.008	3.953
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
C(S)	1.1741	1.1379	1.0433	.9748	.9526	.9342	.0000	.0000	.0000
NA2CO3(C)	73.8447	73.5182	73.2152	73.1829	73.1785	73.1086	68.8319	68.4895	67.9438
NA2S(C)	24.4484	24.6889	24.9120	24.9356	24.9363	24.9363	24.9364	24.9363	24.9363
TOTAL	99.4673	99.3450	99.1705	99.0933	99.0675	98.9792	93.7682	93.4258	92.8801

TABLE VI

EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na_2S - 24.41%
Na_2CO_3 - 73.24
Na_2SO_4 - 1.00
Carbon - 1.338

WATER ADDED: 0.1#/99.9# SMELT

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

PRESSURE: 1.00 ATMOS. PER CENT TOTAL AIR: .0

TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	11.564	29.473	38.077	40.333	44.142	46.750	46.918	46.931	46.678
CO2	7.605	5.017	1.304	.313	.103	.038	.015	.007	.003
H2	51.135	55.532	57.394	57.679	46.769	40.227	40.219	40.174	39.726
H2O	14.547	6.550	1.980	.611	.191	.071	.033	.017	.009
CH4	8.408	3.008	1.196	.527	.171	.069	.040	.025	.016
H2S	6.688	.409	.009	.000	.000	.000	.003	.033	.269
COS	.051	.007	.000	.000	.000	.000	.000	.001	.011
NA2	.000	.000	.000	.000	.044	.081	.059	.037	.028
NA	.000	.000	.003	.210	6.825	12.072	12.492	12.669	13.173
NAH(G)	.000	.000	.000	.001	.021	.038	.044	.048	.053
NAOH(G)	.000	.002	.035	.324	1.733	.652	.180	.057	.021
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
C(S)	29.6999	26.2034	24.0616	23.4190	20.4136	17.1166	16.8598	16.7920	16.7678
NA2CO3(C)	42.9492	30.1943	29.0540	28.2586	12.5749	.0000	.0000	.0000	.0000
NA2S (C)	.4436	9.8339	10.6344	10.6546	10.6552	10.6547	10.6458	10.5412	9.6380
TOTAL	73.0926	66.2315	63.7500	62.3321	43.6437	27.7713	27.5056	27.3331	26.4057

TABLE VII

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

PRESSURE: 1.00 ATMOS. PER CENT TOTAL AIR: 30.0

TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	13.506	28.085	33.717	33.969	34.060	33.884	33.753	33.563	33.040
CO2	10.372	4.555	1.632	1.431	1.482	2.038	2.067	2.031	1.835
H2	15.878	18.714	19.530	19.354	18.249	15.248	14.998	14.558	13.631
H2O	5.275	2.103	.952	1.113	1.390	1.976	2.358	2.626	2.564
CH4	.811	.342	.087	.009	.001	.000	.000	.000	.000
N2	52.325	46.072	44.050	43.874	43.167	41.074	40.960	40.721	39.956
H2S	1.779	.119	.006	.002	.002	.003	.034	.233	.809
COS	.051	.006	.000	.000	.000	.000	.003	.019	.069
S2	.000	.000	.000	.000	.000	.000	.000	.005	.143
NA	.000	.000	.002	.042	.416	1.675	2.158	2.852	4.449
NAH(G)	.000	.000	.000	.000	.001	.003	.005	.006	.011
NAOH(G)	.000	.001	.022	.204	1.232	4.097	3.663	3.383	3.487
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
C(S)	5.6944	1.6441	.0000	.0000	.0000	.0000	.0000	.0000	.0000
NA2CO3(C)	17.8353	12.3677	11.8862	11.4429	8.6792	.0000	.0000	.0000	.0000
NA2S (C)	.0000	4.0243	4.3468	4.3563	4.3585	4.3539	4.2530	3.5629	.7121
TOTAL	23.5297	18.0361	16.2331	15.7992	13.0377	4.3539	4.2530	3.5629	.7121

TABLE VIII

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

PRESSURE: 1.00 ATMOS. PER CENT TOTAL AIR: 60.0

TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	11.123	12.292	12.995	13.676	14.315	14.928	15.290	15.785	16.028
CO2	12.309	11.404	11.144	10.638	10.287	10.439	9.949	9.136	8.841
H2	9.394	8.738	7.936	7.184	6.311	4.941	4.475	4.096	3.978
H2O	4.497	5.617	6.856	7.626	7.939	7.443	7.475	7.063	7.433
CH4	.162	.006	.000	.000	.000	.000	.000	.000	.000
N2	61.440	61.106	60.756	60.549	59.923	58.016	57.779	57.124	56.968
H2S	1.032	.798	.275	.120	.063	.046	.246	.442	.305
SO2	.000	.000	.000	.000	.000	.000	.009	.061	.141
SO	.000	.000	.000	.000	.000	.000	.001	.010	.028
COS	.041	.037	.015	.008	.005	.005	.029	.059	.043
S2	.000	.000	.000	.000	.000	.000	.022	.212	.239
NA	.000	.000	.000	.004	.039	.243	.435	.857	1.151
NAOH(G)	.000	.001	.022	.196	1.118	3.939	4.289	5.154	4.843
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
NA2CO3(C)	11.2151	10.4042	8.4705	7.5931	5.6808	.0000	.0000	.0000	.0000
NA2S (C)	.0000	.5955	1.9922	2.4084	2.5608	2.6017	1.8417	.0000	.0000
TOTAL	11.2151	10.9997	10.4627	10.0015	8.2416	2.6017	1.8417	.0000	.0000

TABLE IX

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

PRESSURE: 1.00 ATMOS. PER CENT TOTAL AIR: 100.0

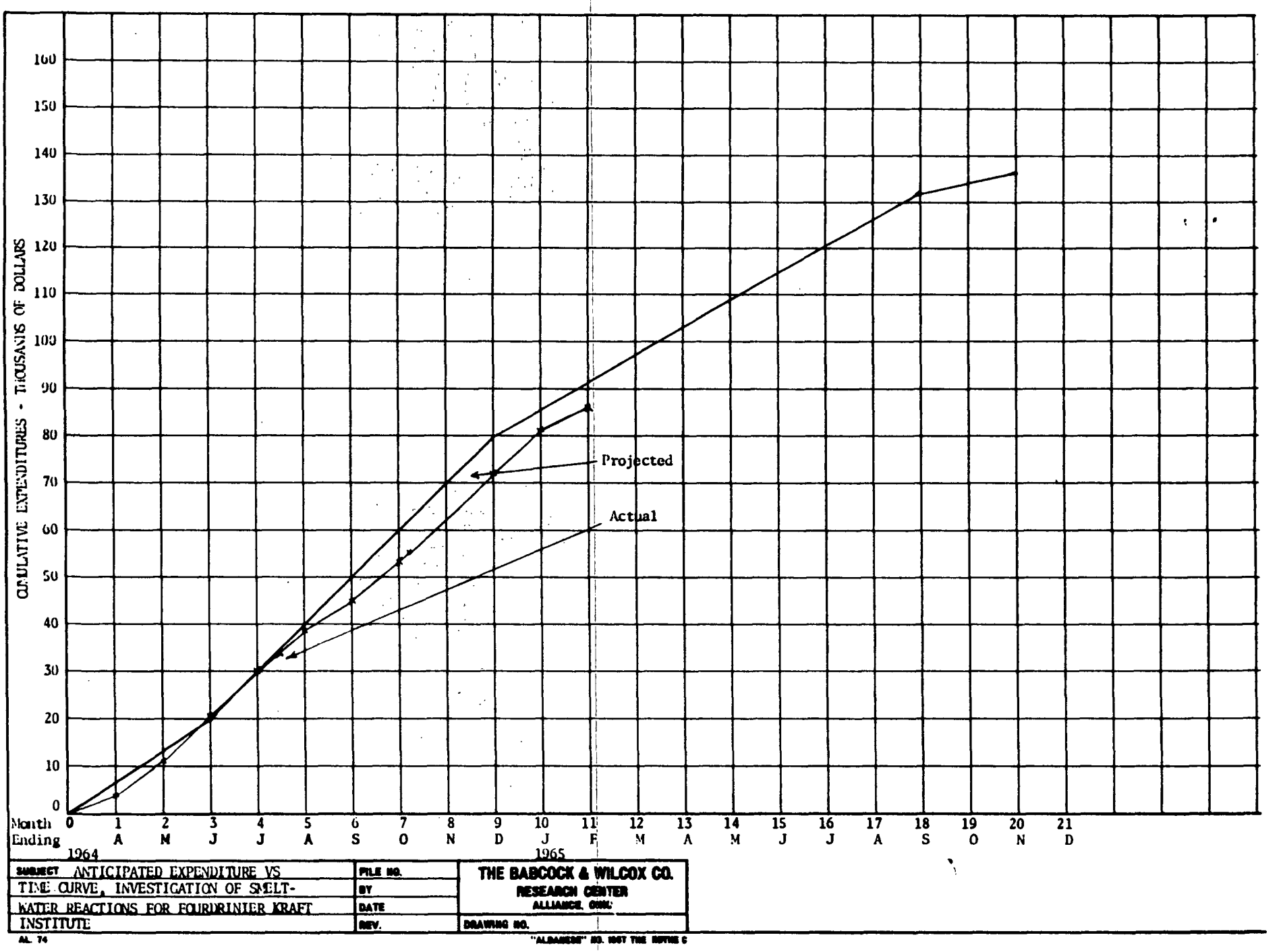
TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES(GASEOUS)					VOLUME PERCENT				
CO	.222	.506	.922	1.387	1.744	1.869	1.448	1.473	1.474
CO2	16.558	16.358	16.056	15.752	15.727	16.262	16.470	16.441	16.433
H2	.329	.471	.600	.676	.638	.477	.290	.257	.228
H2O	10.590	10.549	10.533	10.476	10.075	8.944	8.475	8.533	8.590
N2	71.774	71.695	71.579	71.359	70.693	69.105	68.291	68.271	68.250
H2S	.513	.398	.256	.120	.037	.011	.004	.001	.000
SO2	.001	.003	.010	.027	.052	.128	.703	.708	.708
COS	.012	.014	.013	.008	.003	.001	.001	.000	.000
NA	.000	.000	.000	.001	.009	.050	.096	.143	.202
NAOH(G)	.000	.002	.023	.189	1.018	3.150	4.215	4.167	4.106
SPECIES(CONDENSED)					LBS / 100 LBS OF FEED				
NA2CO3(C)	6.7541	6.4082	5.9427	5.2506	3.6101	.0000	.0000	.0000	.0000
NA2SO4(C)	.9993	1.4596	2.0351	2.5904	2.8993	2.6774	.0000	.0000	.0000
TOTAL	7.7534	7.8677	7.9778	7.8409	6.5094	2.6774	.0000	.0000	.0000

TABLE X

TABLE XI

ANALYSIS OF GAS FROM THERMAL
DECOMPOSITION OF BLACK LIQUOR SOLIDS

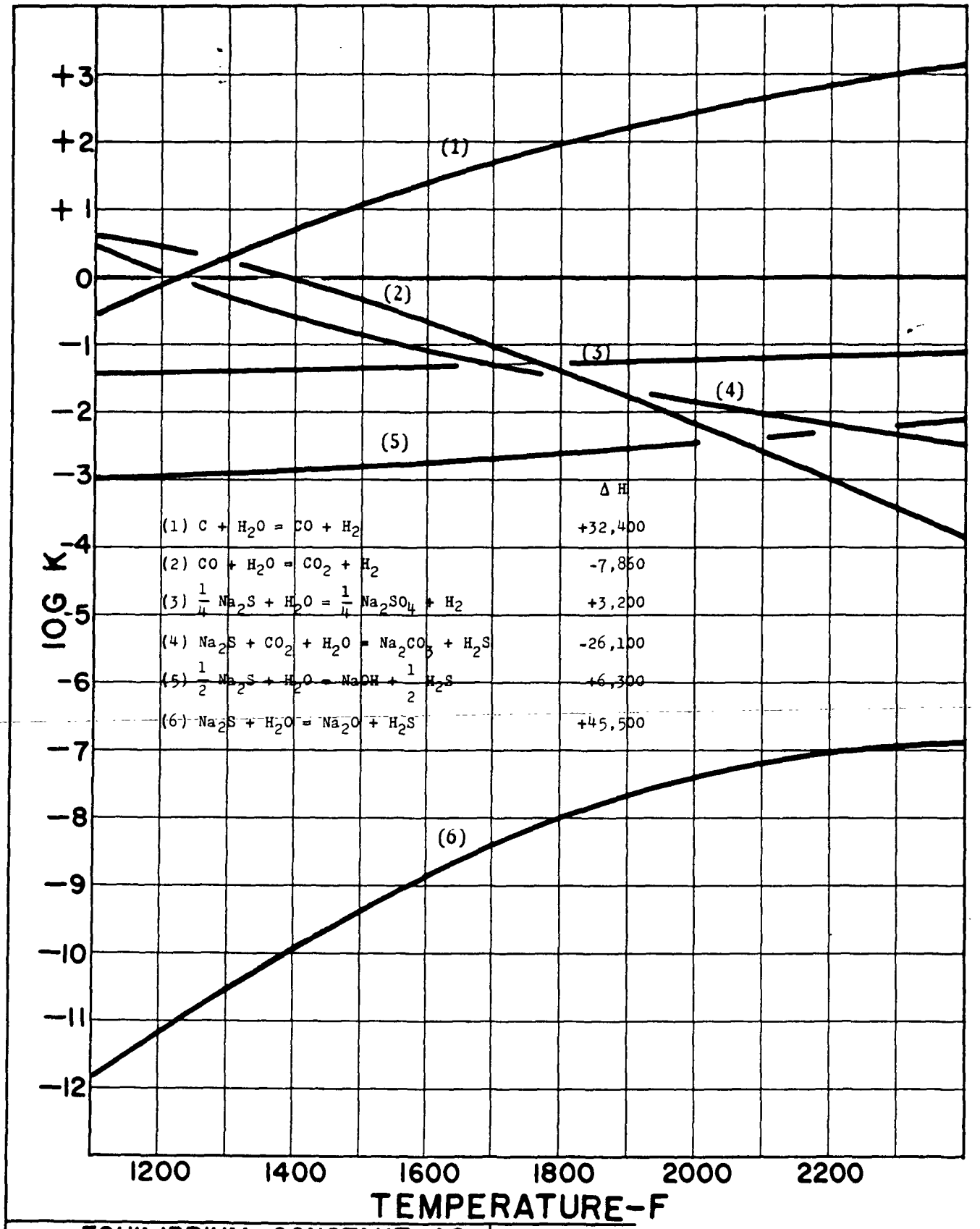
TEMPERATURE °F	600°	800°	1000°	1200°	1400°	1600°	1800°
H_2	Trace	0.9%	8.8%	32.0%	40.0%	36.%	30.4%
CO	32.5%	27.0	21.8	16.5	23.0	41.	54.1
CH_4	1.7	5.2	10.5	13.0	9.2	5.8	4.7
H_2S	11.1	8.3	8.3	4.5	1.8	1.2	0.5
COS	Trace	0.8	1.3	1.6	0.5	0.2	0.2
SO_2	14.9	17.4	14.4	7.6	3.0	0.5	0.5
CO_2	40.0	41.0	35.0	25.0	22.3	15.0	9.5
Volume (STP) cc/gm solids	46.2	63.3	107	151	303	459	720



SUBJECT ANTICIPATED EXPENDITURE VS TIME CURVE, INVESTIGATION OF SMELT-WATER REACTIONS FOR FOURDRINIER KRAFT INSTITUTE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

AL. 74

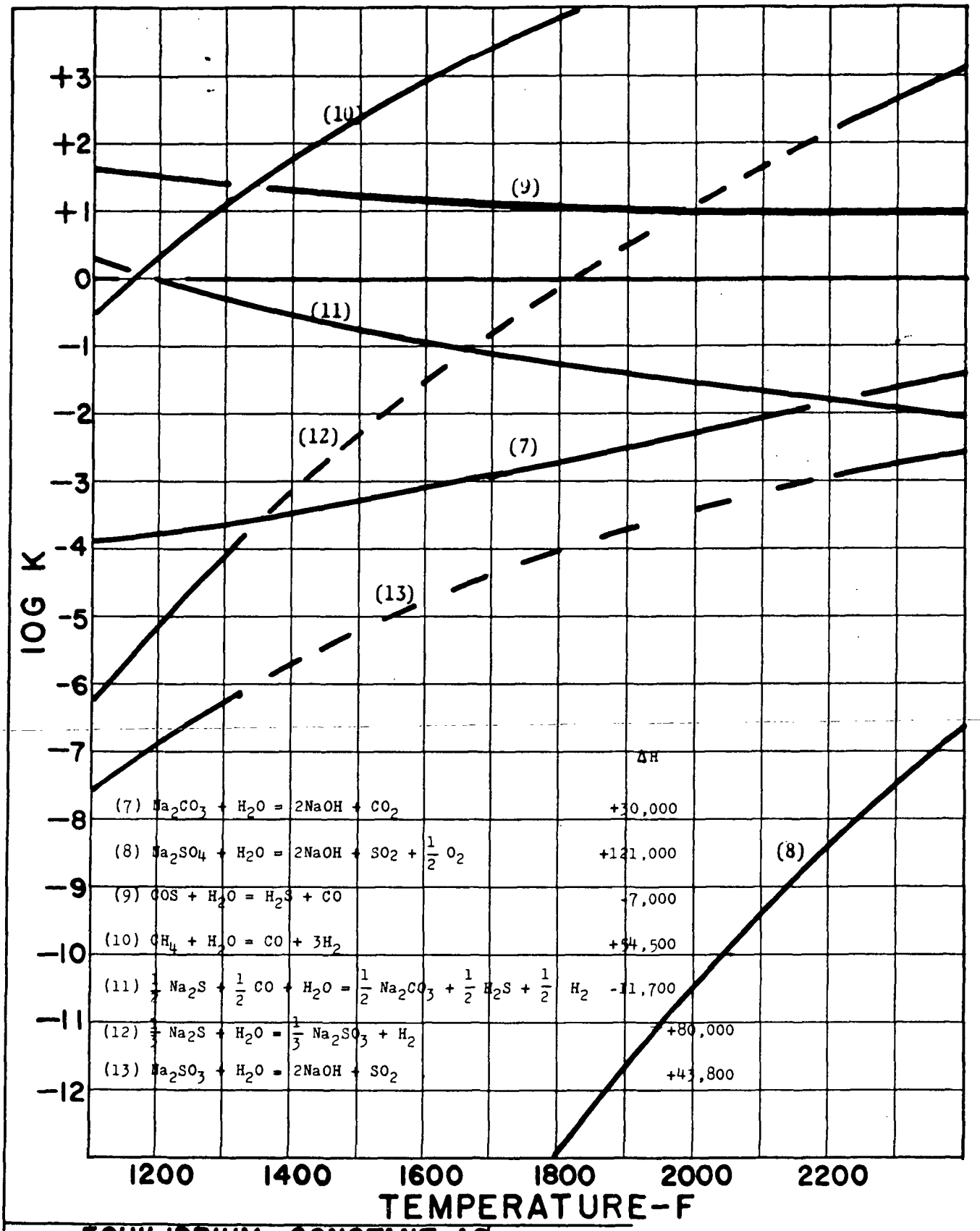
"ALBANENE" NO. 1007 THE BOSTON C



	Δ H
(1) $C + H_2O = CO + H_2$	+32,400
(2) $CO + H_2O = CO_2 + H_2$	-7,850
(3) $\frac{1}{4} Na_2S + H_2O = \frac{1}{4} Na_2SO_4 + H_2$	+3,200
(4) $Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S$	-26,100
(5) $\frac{1}{2} Na_2S + H_2O = NaOH + \frac{1}{2} H_2S$	+6,300
(6) $Na_2S + H_2O = Na_2O + H_2S$	+45,500

SUBJECT EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE	FILE NO.
	BY
	DATE
	REV.

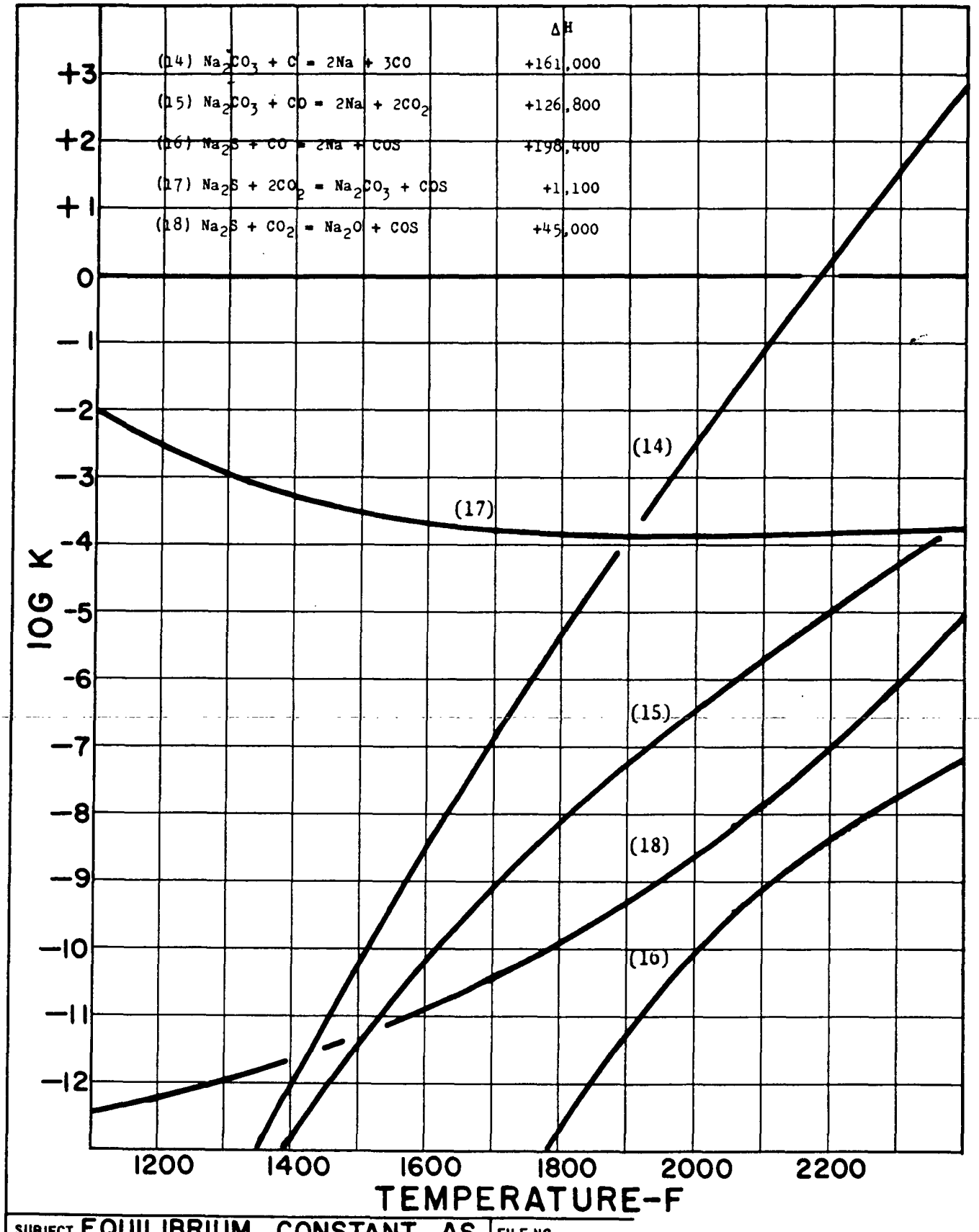
FIGURE 1



	ΔH
(7) $Na_2CO_3 + H_2O = 2NaOH + CO_2$	+30,000
(8) $Na_2SO_4 + H_2O = 2NaOH + SO_2 + \frac{1}{2} O_2$	+121,000
(9) $COS + H_2O = H_2S + CO$	+7,000
(10) $CH_4 + H_2O = CO + 3H_2$	+54,500
(11) $\frac{1}{2} Na_2S + \frac{1}{2} CO + H_2O = \frac{1}{2} Na_2CO_3 + \frac{1}{2} H_2S + \frac{1}{2} H_2$	-11,700
(12) $\frac{1}{3} Na_2S + H_2O = \frac{1}{3} Na_2SO_3 + H_2$	+80,000
(13) $Na_2SO_3 + H_2O = 2NaOH + SO_2$	+43,800

SUBJECT EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE	FILE NO.
	BY
	DATE
	REV.

FIGURE 2



SUBJECT EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE	FILE NO.
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	REV.

FIGURE 3

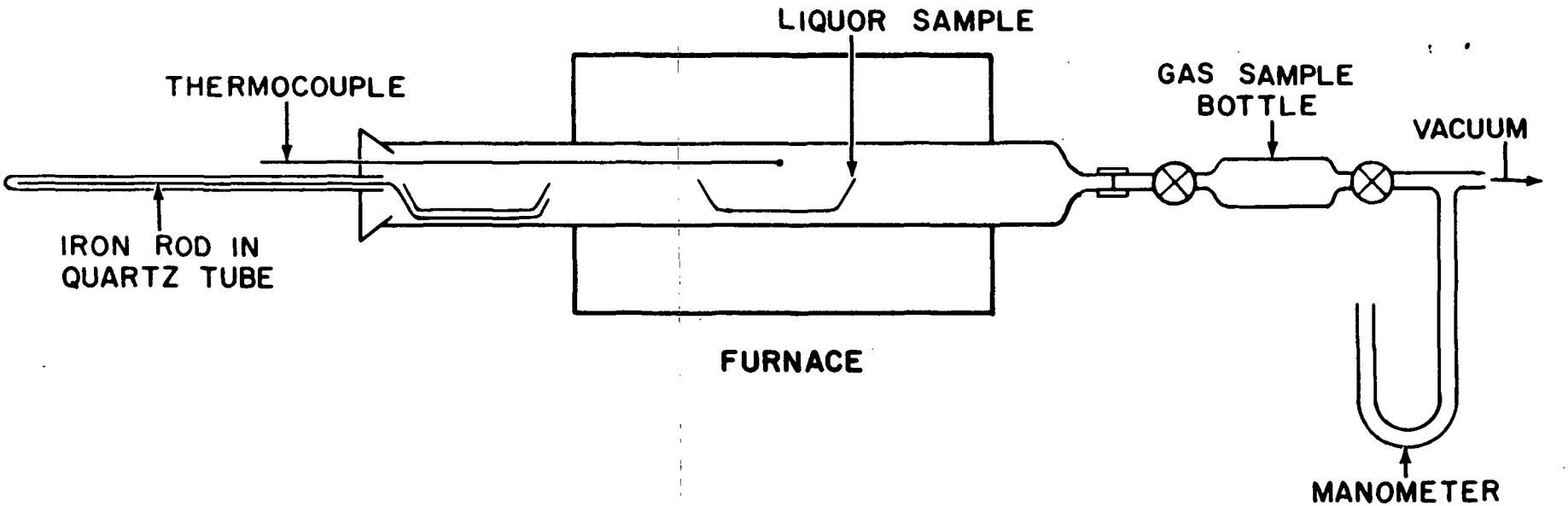


FIGURE 4

BLACK LIQUOR

DECOMPOSITION FURNACE

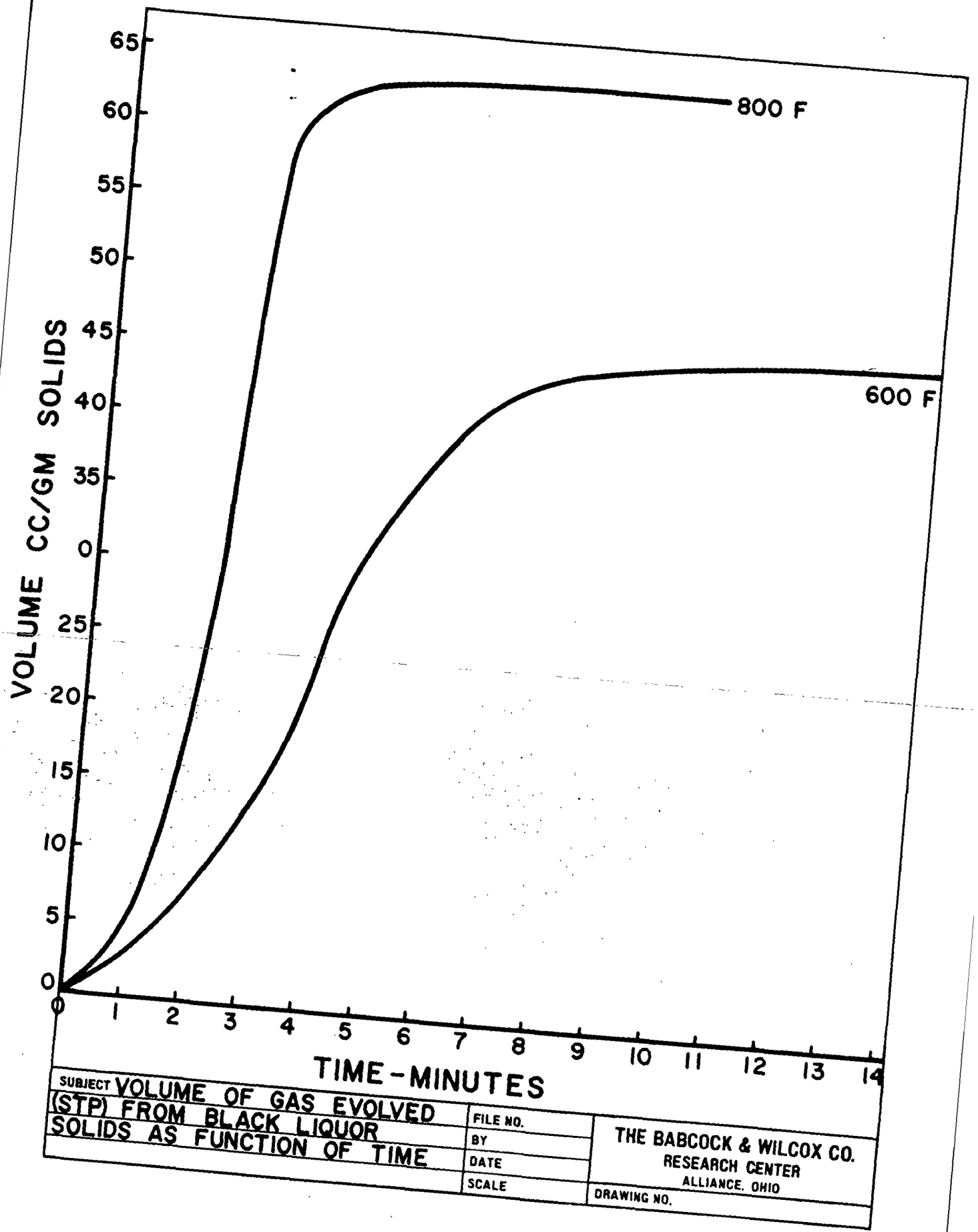
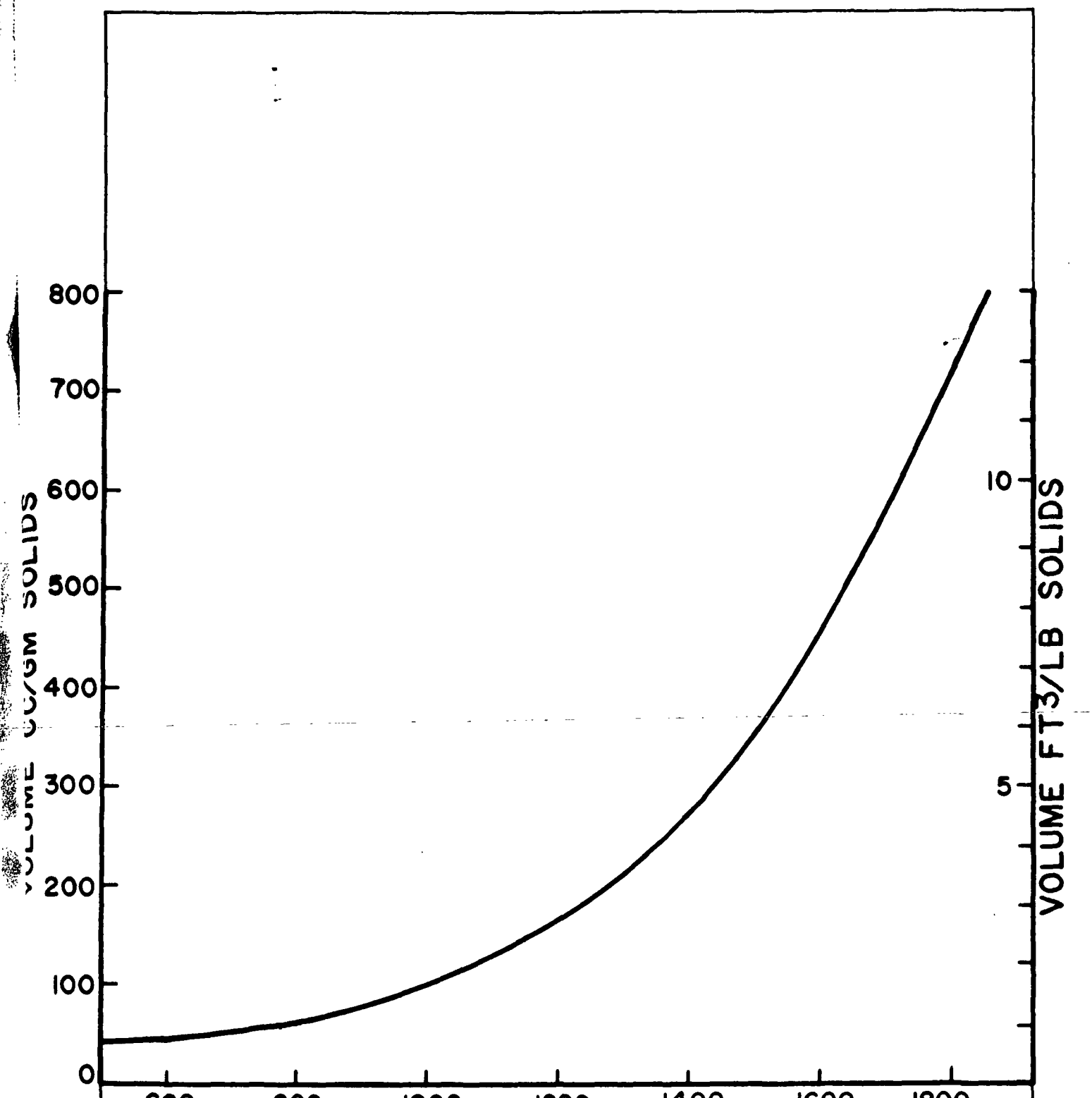
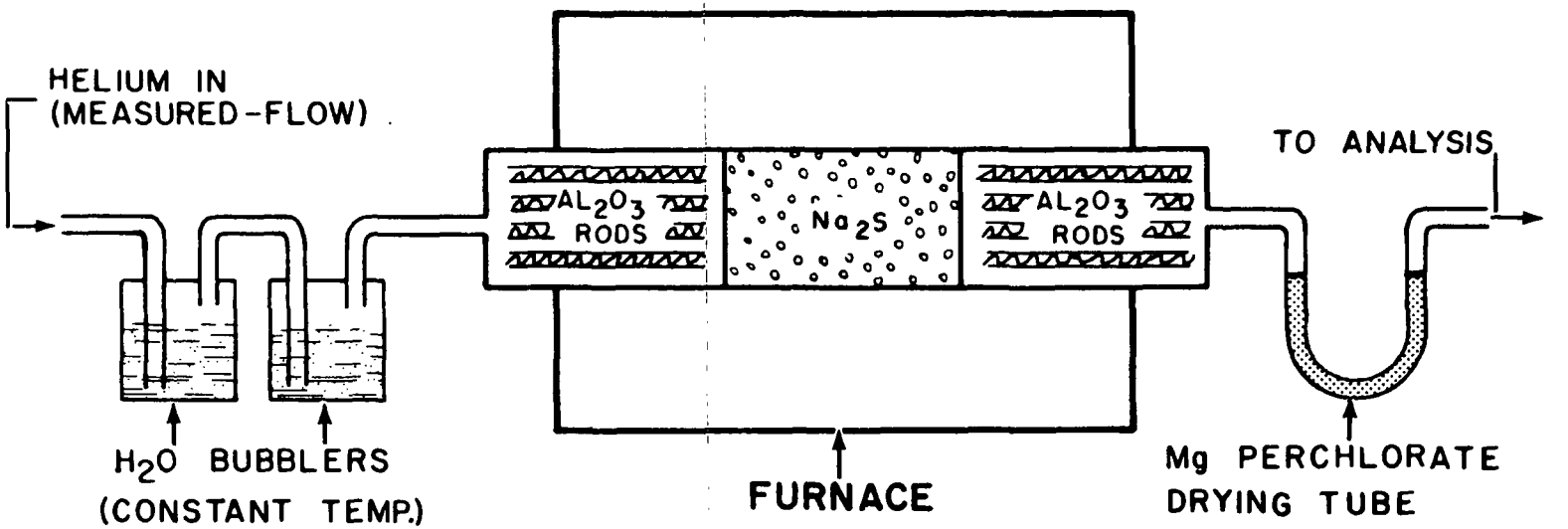

VOLUME CC/GM SOLIDS
65
60
55
50
45
40
35
0
25
20
15
10
5
0
800 F
600 F
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
TIME-MINUTES
SUBJECT VOLUME OF GAS EVOLVED (STP) FROM BLACK LIQUOR SOLIDS AS FUNCTION OF TIME
FILE NO.
BY
DATE
SCALE
THE BABCOCK & WILCOX CO.
RESEARCH CENTER
ALLIANCE, OHIO
DRAWING NO.

FIGURE 5



SUBJECT VOLUME OF GAS EVOLVED FROM BLACK LIQUOR SOLIDS AS FUNCTION OF TEMPERATURE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	SCALE	DRAWING NO.

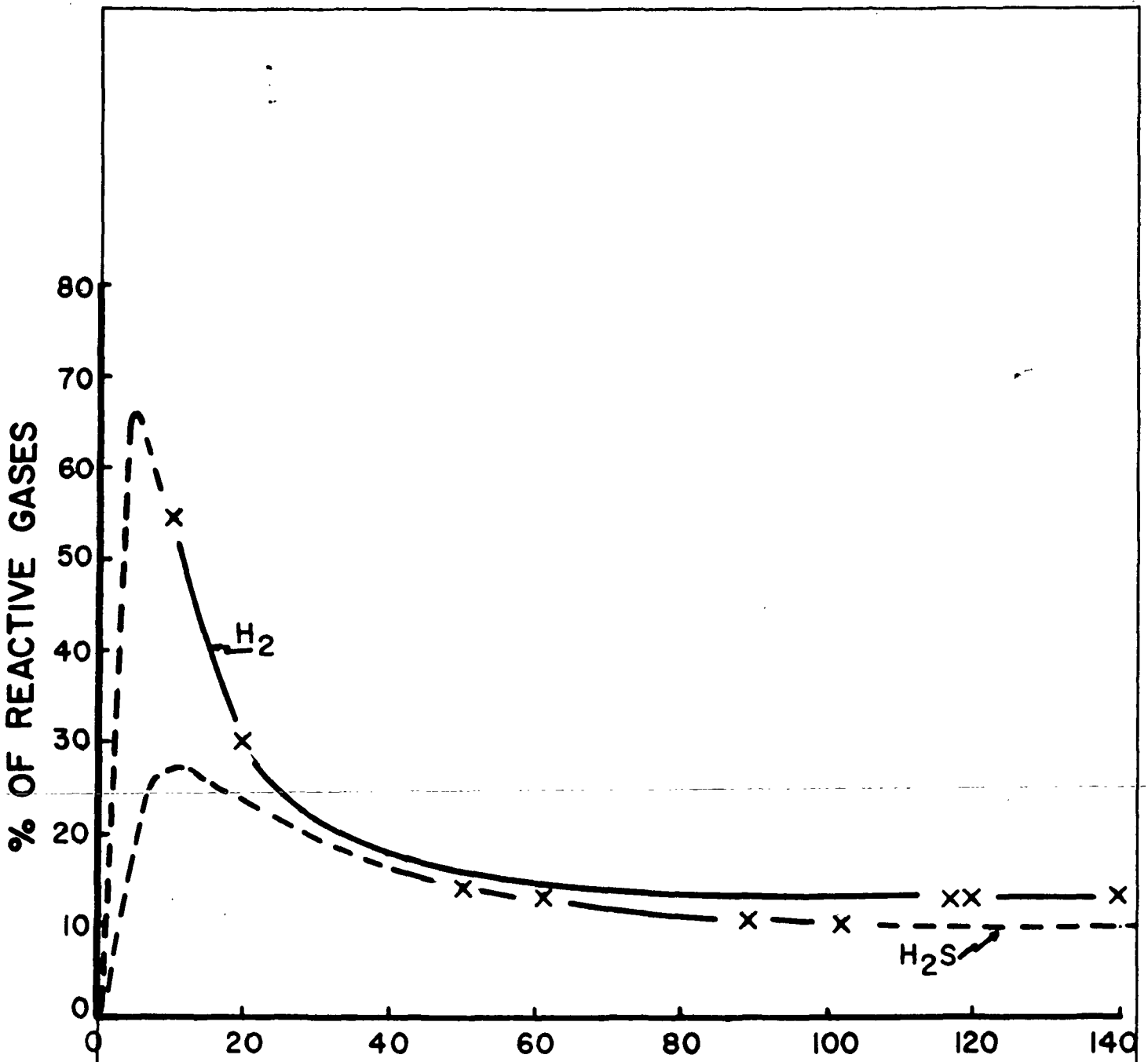
FIGURE 6



TEST APPARATUS

FOR H_2O (VAPOR) - Na_2S (SOLID) REACTION STUDIES

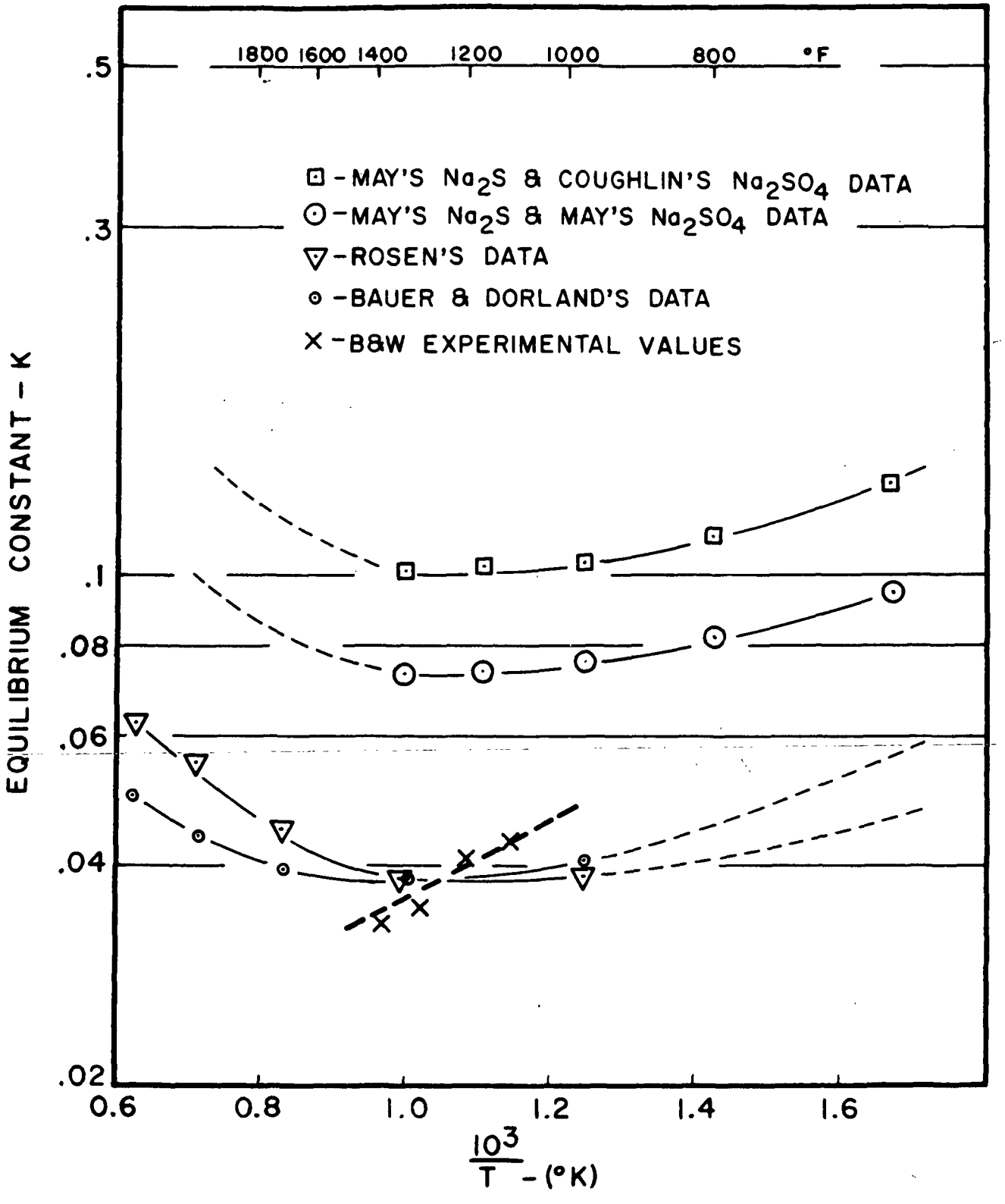
FIGURE 7



YIELD OF H_2 AND H_2S FROM
$H_2O - Na_2S$ REACTION (1650 F)

SUBJECT	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	SCALE	DRAWING NO.

FIGURE 8



EQUILIBRIUM CONSTANT VS $\frac{1}{T}$ FOR

$$\frac{1}{4}\ Na_2S + H_2O = \frac{1}{4}\ Na_2SO_4 + H_2$$

FIGURE 9

TRIMONTHLY PROGRESS REPORT
COVERING WORK FROM NOVEMBER 6, 1964 THROUGH MARCH 5, 1965

to

Dr. H. S. Gardner, Project Coordinator
The Institute of Paper Chemistry

Submitted by
Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

NO. 4 PROGRESS REPORT ON THE COMBUSTION ENGINEERING PROGRAM FOR DETERMINING THE NATURE OF AND REMEDIES FOR EXPLOSIVE REACTION(S) BETWEEN SMELT AND WATER IN KRAFT CHEMICAL RECOVERY FURNACES

Encapsulation Mechanism Theory

(Supporting evidence for some facets of the theory which follows are presented in the later sections on experimental results.)

Liquid water has a uniquely high specific heat (heat capacity) and latent heat of vaporization compared with other fluids. This is due in large part to its hydrogen-bonded structure which greatly restricts molecular movement on heating. The nature of the molten material (metal or ceramic) also is important, and according to this theory, must allow the almost instantaneous generation of a frozen shell having considerable tensile strength when water is placed beneath melt surface at appropriate temperatures for both liquids.

Submerging liquid water beneath melt of proper composition is believed to result in the following concurrent processes:

(a) A very high initial heat transfer rate occurs between molten melt and encapsulated liquid water which increases frozen shell thickness rapidly.

(b) The high heat absorbing capacity of water (and low specific heat of most molten materials) causes a relatively thick containing shell of solid to freeze per unit weight of water compared with other fluid coolants.

(c) A sizeable time delay (on the millisecond scale), compared with immersion of gases or other liquid coolants, occurs during which internal capsule pressure fails to outrace the increasing shell strength (thickness).

The net result of a, b, and c, is that frozen shell thickness forms fastest initially when the pressure inside the capsule is the lowest. Thus encapsulation explosions may be made possible in part by the unique physical properties of water itself. Delay created by racing of these two opposing processes, i.e., the pressure buildup, and increasing shell thicknesses to contain it, allows rapid storage of thermal energy as hot water and steam under pressure in the capsule. Rupture of the capsule liberates this stored energy much more rapidly than it was stored. Mechanical

PV work is done by rapidly expanding steam from the explosion.

An encapsulation explosion in kraft smelt may be analogous in some respects to heating a compressed nitrogen cylinder until a physical explosion occurs. This explosion is due solely to the sudden release of stored thermal energy by rupture of the walls. No chemical change is involved in the process. Here also energy stored at a comparatively leisurely pace during heating can be liberated very rapidly by bursting of the shell. Using this concept, we have postulated a model of the pressure vs. time sequence inside a capsule in kraft smelt to explain what happens, assuming subcritical conditions. These points are illustrated by the theoretical diagram and graphs of Fig. 1:

(1) A volume of water is placed under the surface of the molten smelt at time A. A strong encapsulation shell of frozen smelt forms almost immediately around this submerged volume of water and some surrounding steam blanket, and increases in thickness rapidly.

(2) A sizable induction period AC occurs in which water inside the capsule absorbs heat very rapidly from the surrounding body of hot molten smelt. This heat passes through the thickening frozen shell. Pressure inside the capsule increases rapidly during this period because of the efficient heat transfer caused by a large ΔT and a relatively thin shell.

(3) Shell strength (thickness) to contain this pressure increases less rapidly after the initial containment shell forms due to: (a) a decreasing temperature differential between the smelt and water, and (b) the increasing distance required for heat of fusion to travel to the water.

(4) Shell rupture B (explosion) occurs when pressure build-up wins this race, releasing steam and/or hot water in atomized condition into the main body of surrounding molten smelt. Capsule pressure quickly assumes atmospheric value, following line BD.

(5) PV energy stored in the capsule is liberated as an explosion wave in the very brief time interval CD. Compare this with much longer interval AC required for energy storage.

Quick energy release is an inherent characteristic also of condensed phase explosives like TNT, which on detonation creates large volumes of gases almost instantaneously by chemical reactions. Here useful mechanical work is accomplished due to: (a) the tremendously rapid (in the millionth of a second range) release of energy and (b) the concentration of energy release in the small volume occupied by the explosive itself, rather than to an inherently large quantity of energy produced from a unit weight of

the explosive. The damage effects of physical and chemical explosions are similar in type since both are caused by rapid release of gases under high pressure. The release rate from encapsulation explosions has been found to be almost a thousand times slower than that from TNT in the small scale tests conducted to date so that the two would probably not be comparable in extent of damage. Both, however, free a large amount of energy per unit volume of original exploding (condensed phase) material. Mechanisms of chemical and physical explosion processes are different in some important respects. For instance the proposed existence of an encapsulation shell in physical explosions provides hope for a successful plant remedy as outlined in a later section of this report.

Experimental

(A) High Speed Movies

Mr. Tung Nathan, Mr. Charles Norton, and Mr. Douglas Wayne of this laboratory developed the successful photographic and explosion techniques described in this section.

It was decided to take high speed color movies of water injections into molten kraft smelt in order to gain a better idea of what happens in an explosion and the detailed sequence of events preceding it. Perhaps one could even photograph a capsule before it exploded if light could be made to penetrate far enough below smelt surface. Pictures taken with an ordinary movie camera at 32 frames per second were not nearly fast enough to reveal the necessary details of an explosion process. A model K1004 Hycam motion picture camera (16mm. x 400 ft.) was rented. It can vary taking speed from 10 to 20,000 pictures per second without changing the motor. Tri X black and white film (ASA 200) produced pictures too grainy to be useful. Also it did not give the details provided by color film. Most of the pictures to date have been on High Speed Ektachrome ERB (ASA 125, which is increased to 250 by special development). Use of 400 foot lengths of film allowed placing both injection and explosion on one reel at a speed of 5600 frames per second.

Manual synchronization of the explosion to starting of the camera was employed effectively. Photoflood lights and several types of ordinary stand-mounted photographic flood lights did not give enough illumination. Next, a series of four Sylvania FF33 long duration flash lamps were placed on four corners of a square surrounding frame less than a foot away from the crucible of molten smelt. They were fired by a cam-operated sequence timer after water injection so that each (after the first) would fill in the "tail off" period of its predecessor. This arrangement provided almost enough light to give the needed details, but the shifting direction of illumination as each bulb fired produced confusing shadows. The problem of gaining sufficient illumination has been a difficult one at the high speeds used. The next efforts will be made as suggested by the Bureau of Mines using a

movie type carbon arc projector, or a specially designed high intensity light with condensing lens system to concentrate light on the surface of smelt in the crucible. Prints of some of these pictures will be included in the next progress report. Movies will be shown at the next meeting of the Advisory Technical Committee.

Injections of room temperature 10% green liquor (10% kraft smelt dissolved in water) were found to increase the certainty of an explosion on first injection, when in addition the smelt was cooled to 1600°F. This is about mid-point of the temperature range in which kraft smelt explodes with successive water injections.

Although improvement in movie quality, particularly lighting, is desirable, the explosion and prior events were correctly framed in speed. The following points were established from careful examinations of three films:

(1) No flame was evident in any explosion or in events leading to it. Only glowing particles of finely divided smelt were observed during all explosions.

(2) There was a fairly consistent 0.030 second (30 milliseconds) delay between the completion of green liquor injection and the resulting explosion. The surface of the smelt was turbulent following a water injection.

(3) The explosion itself was very rapid and required only about 2 milliseconds.

(4) Explosions were initiated from a source of limited area (approx. 1/2" diameter) below smelt surface, exactly where liquor injection had been made.

All of these observations fit the theoretical model proposed for a physical encapsulation explosion. Incidentally, it has been found that the "firecracker-like" odor produced by explosions is due to smelt dust and is eliminated almost entirely when the observer wears a dust filter mask. The smelt used (30% Na_2S) was opaque over the entire molten temperature range 1450° to 2000°F., so it was not possible to see through any appreciable depth. Other compositions of materials, like 80% Na_2CO_3 with 20% NaCl, also explode violently on water injection and are considerably more transparent. It may be possible to photograph an encapsulation produced by injecting water into melts like this one.

(B) Pressure Wave Measurements

(Mr. Charles Norton, Research Engineer, shared in the development of techniques and data reported in this and following

sections). Considerable interest lies in accurately measuring the speed and amplitude of shock waves produced by explosions from water injected into molten smelt. Effort has been made to keep explosions down to a scale which will not damage the plywood explosion barrier or operating personnel. This has been accomplished by regulating the volume of water to individual successive injections of 3 cc., about 60 drops. The violence produced is surprisingly great from even this small quantity of water. It increases as the smelt temperature at which explosions take place increases within the 1470-1670°F range mentioned in earlier reports. This range can be altered by changing the smelt composition.

The pressure wave measurements have been continued using the Visicorder with a new high speed drive. Increased chart speed has allowed a more accurate assessment of the duration of pressure waves produced. They have averaged 1 to 3 milliseconds, which is about a thousand times slower than waves from condensed phase chemical explosives. This direct transducer measurement agrees well with the photographically calculated value reported in section (A). It is possible that these speeds may scale up when larger injections are used in the spherical high pressure explosion vessel.

Mr. R. W. Watson of the Bureau of Mines mentioned on our February 3-4 visit that there is strong reason to doubt the efficient transfer of shock wave energy from molten smelt to air. Thus the current technique for estimating explosion pressures at the capsule itself may have to be modified so that a metal rod transmits this wave to a directly-coupled transducer diaphragm. In the present state, however, the transducer setup does permit valid conclusions about the number of explosions, the time between them, their speed, and their relative intensity.

(C) Effect of Water Temperature and Dissolved Smelt

Several further experiments on the effects of composition of the aqueous phase and its temperature seemed in order. Table 1 which follows shows the results from successive 3 cc. injections of aqueous material in molten 1800°F. synthetic kraft smelt (30% Na_2S) until an explosion or solidification resulted.

TABLE 1

Solution Injected	Results	Smelt Temp. (°F) for Explosion
1) Blank - 68°F. Water	Violent explosion	1650
2) Blank - 68°F. Water	Violent* explosion	1585
3) 176°F. Water	Violent* explosion	1503
4) 187°F. Water	None	-
5) 203°F. Water	None	-
6) 203°F. Water	None	-
7) 205°F. 10% Green Liquor	Violent*explosion	1640
8) 212°F. 10% Green Liquor (tube leak)	Three moderate explosions	Unknown

*Shattered crucible

Runs No. 1 and 2 reconfirmed many previous experiments showing the violent explosions which almost invariably result if cool water is suitably submerged beneath the surface of molten smelt. Runs 3, 4, 5, and 6 established the fact that water hot enough will not explode under the same conditions of mixing with smelt. These results posed the question of how hot water from a ruptured boiler tube can cause explosions. Run No. 7 in which hot green liquor made by dissolving 10% smelt in water was injected into smelt showed that inclusion of dissolved salts can override the explosion-preventing effect of very hot water. Run No. 8 with 212°F. 10% green liquor added in a continuous stream (102 cc/15 seconds) to the surface of the molten smelt (rather than below it) to simulate a small tube leak gave three moderate explosions in quick succession. This confirmed results of the previous experiment which used forcible injection of green liquor below smelt surface.

Results of these tests agree exactly with conclusions of the previous 1956 study (1) on dissolving tank explosions. I.e., hot water (if it is hot enough) lessens smelt-water explosions. Salts dissolved in the water make its explosive reaction more violent with molten smelt. These results also imply that water standing on smelt in a chemical recovery furnace probably increases the chance of an explosion with time (within limits) due to:

(a) increased dissolved smelt content in the water.

(b) reduced temperature of the water.

(c) reduced temperature of the smelt to 1670°F, but above 1470°F.

(D) Smelt Additives

We believe that one of the most promising remedial measures to physical smelt-water explosions in chemical recovery furnaces is the maintenance of a small proportion of suitable material in smelt to render it non-explosive on accidental contact with water. As mentioned in previous reports, soda smelt (sodium-chloride free) consisting essentially of sodium carbonate, has never resulted in an explosion on contact with water under any plant or laboratory conditions.

Based on the physical encapsulation mechanism, it seemed reasonable to search for an "alloying" agent for the ceramic (kraft smelt) which would weaken solid smelt structurally and hence any encapsulating shell of frozen smelt which could form around a volume of water. In this manner the capsule walls would lack sufficient tensile strength to permit build-up of dangerous explosion pressures when water was introduced.

The true origin of the strength[2] of a metal or ceramic involves the forces or bonds between atoms. However, because of defects or imperfections which lead to high local stress concentrations when force is applied, the theoretical strength is never measured in an actual test. There have been numerous indications that impurities have a marked effect upon the mechanical properties of ionic crystals. However very few systematic studies of "alloying" additions to ceramics have been made. Recent investigations by others have shown that ceramic "alloys" behave in the same way as their metallic counterparts. Additions of small (as low as 0.1%) of foreign materials can either strengthen or weaken polycrystalline ceramics.

It was with this thought in mind that we began a systematic trial of additions to synthetic kraft smelt containing 30% Na_2S. A large variety of compounds of various elements in the periodic table have been tried. Effort has been made to vary widely the cation & anion size and charge to modify solid state strength. Dr. A.R.C. Westwood, Associate Director of the Research Institute for Advanced Studies (Baltimore, Md.) who is employed as a consultant on the project, suggested adding other alkali metal carbonates which have multiphase transformations on cooling. These may introduce discontinuities in the crystals and thereby form natural cleavage planes. Most additive candidates were chosen to meet the following qualifications: non-toxic, inexpensive, readily available, and non-interfering with the pulping and recovery cycle. The last qualification may prove the most difficult to meet. It will depend on the proportion required, whether the alloying agent is naturally eliminated in some part of the cycle, and the chemical changes involved in its transport through the various liquor streams. Here, an in-plant test for a successful laboratory-tested candidate may be required for final judgement about its effects on chemical recovery and pulp quality.

The general method of screening an additive was simply to melt 5% of it with the smelt, blend thoroughly and make a succession of 3 cc. injections of room temperature water from 1800° throughout the explosive range of smelt temperatures, approx. 1470-1670°F. The violence of the interaction(s) and the smelt temperature at which they occurred were recorded to compare effect of various additives.

Investigation of the change of physical properties is being made on cooled samples of the smelt for additives which radically affect the violent explosive behavior of molten smelt when water is injected into it.

A large number of smelt additives have been tested for explosion-preventing characteristics. These are listed in appended Table 2. It seemed feasible that a material which increased explosion tendency at one concentration in smelt might lessen it at another. Promising candidates were therefore tested over a range of concentrations. Generally the effective additives caused one of two changes in smelt-water interactions: either

they prevented explosions or they delayed the explosion to a lower (less violent) smelt temperature range. Usually, 15 or more 3cc room temperature water injections were necessary to solidify the smelt if no explosion resulted. Tests are grouped according to the major element involved.

Several conclusions may be drawn from this long list of compounds and results. Some compounds of the following elements appeared to have the tendency to lessen explosive violence: aluminum, calcium, cerium, chromium, cobalt, iron, magnesium, manganese, nickel, and strontium. Of these, aluminum and calcium seem particularly attractive because of effectiveness and price. The identities of both cation and anion of a compound were evidently important in determining effect of an additive. For instance, 5% calcium sulfide (#27) made explosions milder while 5% calcium fluoride (#28) produced one of the most violent explosions to date. Halides (chlorides, bromides, fluorides, etc.) invariably made smelt much more violent. Results from duplicate tests with a given additive were not entirely reproducible. It is believed that reproducibility will improve when the new automatic water injector is installed to replace the current manually-powered hypodermic syringe.

Changing cations also definitely modified the nature of the explosion. For instance 5% cadmium sulfide (#24) produced very violent explosions while 5% nickel sulfide (#74) gave only mild pops on 3 cc injections. There was evidence of an optimum range of concentrations for some materials. For instance in runs #73-76, nickel sulfide which retarded explosions at 2.5% and 5%, intensified them at 10%.

Perhaps the most promising lead is sodium alumnate ($NaAlO_2$) tested in runs #11-18. This material noticeably increased smelt viscosity in concentrations as low as 1.25%. It was effective as low as 0.2% in retarding explosions if injections of water were made in slow succession, allowing each to evaporate before adding another.

Run #16 was made with water injections spaced so closely that one was added before its predecessor had evaporated from smelt surface. This produced a violent explosion at 1560°F. smelt temperature. Such behavior suggested that water on the smelt surface had dissolved smelt and the green liquor created had been forced beneath the smelt surface by a subsequent water injection. Runs #17 and #18 made using 10% green liquor with smelt containing 1 and 5% $NaAlO_2$ (which had been adequate to prevent explosions with slowly spaced water injections) confirmed (a) the higher violence of green liquor injections and (b) the ineffectiveness of $NaAlO_2$ to prevent explosions with this coolant. A successful smelt additive would have to prevent explosions with green liquor. Nevertheless, $NaAlO_2$ is an interesting additive to study. Its modification of smelt properties is being examined in the hope that more complete knowledge of the inhibiting mechanism may facilitate finding a better inhibitor. $NaAlO_2$ is readily soluble in smelt. A material soluble in aqueous alkaline solution might

be circulated unchanged through the pulping and recovery cycle, whereas those which form insoluble sulfides would be precipitated out in the green liquor dissolving tank. Much more makeup and/or processing would be required for this latter class of materials. Results from runs #55-64 implied that longer "cooking", i.e. maintenance in a molten condition, may have reduced $MnSO_4$ to MnS by reaction with the graphite crucible. A five minute cook was the standard procedure.

Strength of an Encapsulation Shell

Dr. A. R. C. Westwood thought it reasonable to expect greatly increased tensile strength of sodium carbonate due to various alloying agents employed and quoted as a parallel the 100-fold enhancement of the tensile strength of iron by suitable alloying additions. He mentioned also a rough figure of 25-fold additional improvement in the normally low tensile values of ceramics by reduction of surface imperfections (due to processes like the Joffe effect discussed in an earlier report) and also to the fine crystalline structure produced by very rapid chilling inherent in the encapsulation process.

A recent investigation of the effect of sodium chloride as an alloying agent on the compression strength of sodium carbonate has showed a direct parallel with the behavior of sodium sulfide in sodium carbonate reported earlier. Presence of 20% sodium chloride or 20% sodium sulfide in sodium carbonate makes the blend react explosively to injection of water. The compression strengths and hardness of $NaCl$-Na_2CO_3 blends are given in Table 3 which follows:

TABLE 3

	Composition Na_2CO_3-%-NaCl		Compression Strength (psi)	Hardness (Vickers Pyramid No.)
1)	100	0	997	9.9
2)	92.5	7.5	1860	17.9
3)	86.5	13.5	4800	20.1
4)	78.4	21.6	6060	18.0

Thus the strength of a sodium carbonate - sodium chloride blend (78.4 - 21.6) is more than six times that of sodium carbonate alone and its hardness is also greatly increased by such alloying.

Future Work

The next item for laboratory work is a further sharpening of photographic technique based on suggestions from Mr. Frank C. Gibson, Mr. R. W. Watson, and Mr. J. E. Hay of the Bureau of Mines so that more detail is shown, especially of the capsule itself beneath smelt surface. Next, synthetic capsules of Pyrex glass and other materials will be made, immersed in smelt, and photographed, to see if parallel explosion behavior is exhibited. Ice pellets will also be tried for injection instead of water---as suggested by Dr. H. S. Gardner and the Bureau of Mines. The computer program for heat transfer into encapsulated water should be finished next month. This is expected to extend knowledge into a highly important area only postulated about before. Scaled-up explosion work in the spherical explosion test vessel will allow a more accurate separation of chemical from physical explosion energy than possible with currently used equipment.

Major emphasis will be placed on an exhaustive search for smelt additives effective against green liquor injection. Better knowledge of the reasons for even partially effective ones like sodium alumnate will no doubt facilitate the quest for practical anti-explosion additives for a chemical recovery furnace. Experiments will be made to produce very rapidly chilled smelt shells on which to determine physical properties. One way is to dip a hollow open-top water-filled aluminum or copper cylinder briefly into smelt to cast thin shells of smelt for strength and "metallographic" examinations. Further improvements in pressure wave measurement suggested by Mr. Frank C. Gibson of the Bureau of Mines will also be made.

Expenditures on the C.E. Smelt-Water Explosion Study

Costs (cumulative) of the Combustion Engineering, Inc. study as of December 31, 1964 are itemized as follows:

Labor	$20,350
Overhead	33,553
Materials	24,574
TOTAL	$78,477

The amount billed to the sponsors as of December 31 was $65,971.88. The actual rate of expenditure and that proposed are compared on the appended graph. The bills from purchase of several major items of equipment have caught up with billing so that the accumulated costs are running closer to estimated ones.

Wharton Nelson

WHARTON NELSON
Senior Project Engineer
March 5, 1965

REFERENCES

(1) "What Causes Dissolving Tank Explosions?" by Wharton Nelson and E. H. Kennedy, Paper Trade Journal, July 16, pp 50-56 and July 23, pp 30-32, 1956.

(2) "Status of Ductile Ceramics Research" by Earl R. Parker, "Properties of Crystalline Solids", ASTM Publication No. 283, pp 52-65.

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TABLE 2

SMELT ADDITIVES TRIED TO DATE

	ADDITIVE	%	EXPLOSION	SMELT TEMP. (°F) FOR EXPLOSION
1 -	None	0	Violent	1650
2 -	"	0	Violent*	1585
3 -	$AlPO_4$	5	Mild Pops	-
4 -	"	10	Sharp Expl.	1480
5 -	Al silicate (kaolin)	5	Violent*	1550
6 -	$Al_2(SO_4)_3$	5	Pops	-
7 -	"	5	Moderate	1500
8 -	"	10	None	-
9 -	Al_2O_3	5	Violent	1600
10 -	"	5	Mild	1710
11 -	$NaAlO_2$	5	Pops (viscous)	-
12 -	"	2.5	None (sl. viscous)	-
13 -	"	1.25	Mild Pops	-
14 -	"	0.5	None	-
15 -	"	0.2	Mild	1460
16 -	"	0.5	Violent (Injection in rapid succession)	1560
17 -	"	1	Violent (10% green liquor)	1600
18 -	"	5	Violent (10% green liquor)	1600
19 -	Sb_2S_3	5	Mild	1610
20 -	$Ba(OH)_2$	5	Violent	1570
21 -	H_3BO_3	5	Violent	1640
22 -	$Na_2B_4O_7$	5	Mild	1630
23 -	NaBr	5	Very Violent	1725
24 -	CdS	5	Very*Violent	1575
25 -	CaO	5	Mild	1430
26 -	$CaSO_4$	5	Moderate	1520
27 -	CaS	5	Moderate	1535
28 -	CaF_2	5	Very Violent	1650
29 -	$CaCO_3$	5	Moderate	1470
30 -	"	7.5	Moderate	1470

*Crucible was shattered

Table 2 (continued)

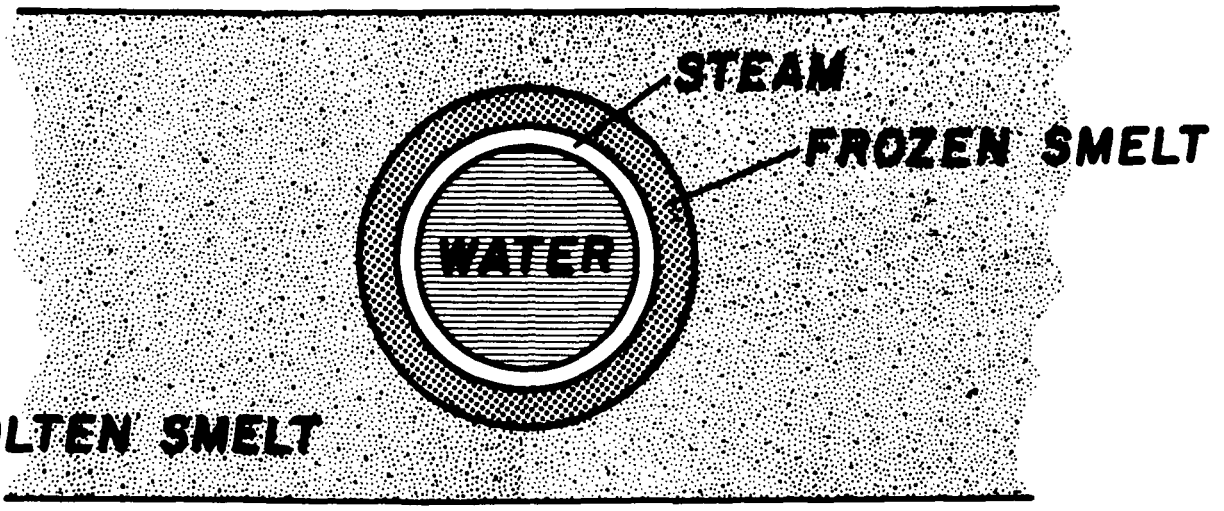
	ADDITIVE	%	EXPLOSION	SMELT TEMP. (°F) FOR EXPLOSION
31 -	$CaCO_3$	10	None	-
32 -	Carbon (fine)	5	Mild	1590
33 -	CeO_2	5	Mild	1435
34 -	"	10	Mild	1550
35 -	Cr_2O_3	5	Violent	1615
36 -	$Cr_2(SO_4)_3$	5	Moderate	1550
37 -	Na_2CrO_4	5	Mild	1510
38 -	Co_2O_3	5	Moderate	1510
39 -	CoS	3.9	Mild	1625
40 -	"	10	Muffled	1700
41 -	$CoSO_4$	5	Violent	1500
42 -	CuO	5	Moderate	1625
43 -	FeS (fine)	5	Moderate	1695
44 -	$Fe_4(P_2O_7)_3$ (pyro)	5	Moderate	1430
45 -	Fe_3O_4	5	Moderate	1720
46 -	Green Liquor Dregs	5	Moderate	1620
47 -	Pb_3O_4	5	Violent	1460
48 -	Li_2CO_3	5	Violent	1730
49 -	Li_2SO_4	5	Mild spits	-
50 -	$MgSO_4$	5	Mild	1550
51 -	MgO	5	Violent	1450
52 -	Mg silicate (Talc)	5	None	-
53 -	"	5	Mild	1560
54 -	$MgCO_3$ (fine)	5	Violent*	1580
55 -	$MnSO_4$	2.5	Violent	1615
56 -	"	5	Moderate	1485
57 -	"	5	Pops	-
58 -	"	5	Violent	1685
59 -	"	5 (25 min. cook)	Mild	1585
60 -	"	20 (25 min. cook)	Very*Violent	1600
61 -	"	10	Mild	1425
62 -	MnS	2.5	Violent	1610

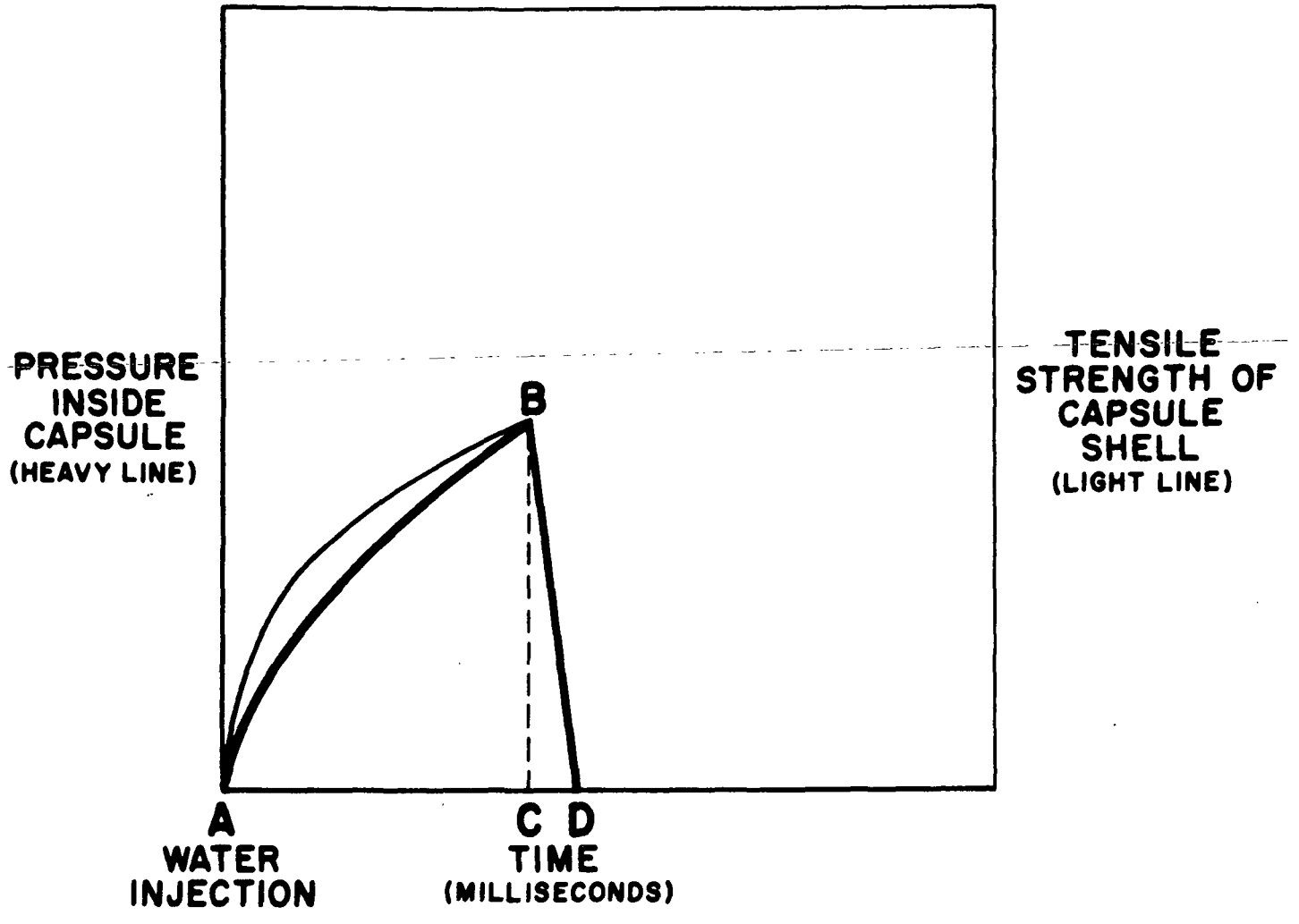
Table 2 (continued)

	ADDITIVE	%	EXPLOSION	SMELT TEMP. (°F) FOR EXPLOSION
63 -	MnS	5	Mild	1630
64 -	"	10	Violent*	1640
65 -	Mn Acetate	5	Moderate	1470
66 -	" "	5	None	-
67 -	$MnCl_2$	5	Violent	1660
68 -	$MnCO_3$	5	Moderate	1490
69 -	"	10	Violent	1460
70 -	MoO_3	5	Violent	1560
71 -	Ni Acetate	5	Violent	1675
72 -	$NiSO_4$	5	Moderate	1485
73 -	NiS	2.5	Mild	1590
74 -	"	5	Pops	-
75 -	"	5	Pops	-
76 -	"	10	Very Violent	1675
77 -	Ni Titanate	5	Mild	1500
78 -	NiO	5	Moderate	1525
79 -	Na_3PO_4	5	Violent	1500
80 -	K_2CO_3	5	Violent	1730
81 -	"	26	Expl. with ea. G.L. inj.	-
82 -	"	69	"	-
83 -	K_2SO_4	5	Violent	1595
84 -	Na_2SiO_3	5	Violent	1580
85 -	SiC	5	Violent	1740
86 -	SiO_2 (fine)	5	Moderate	1710
87 -	SrO	5	Mild	1580
88 -	Na_2SO_4	10	Moderate	1450
89 -	"	13	Very Violent	1585
90 -	Na_2S	8-40	Violence incr. % Na_2S	
91 -	SnO_2	5	Violent	1580
92 -	Na_2SnO_3	5	Moderate	1620
93 -	TiO_2	5	Violent	1630
94 -	Na_2WO_4	5	Violent*	1600

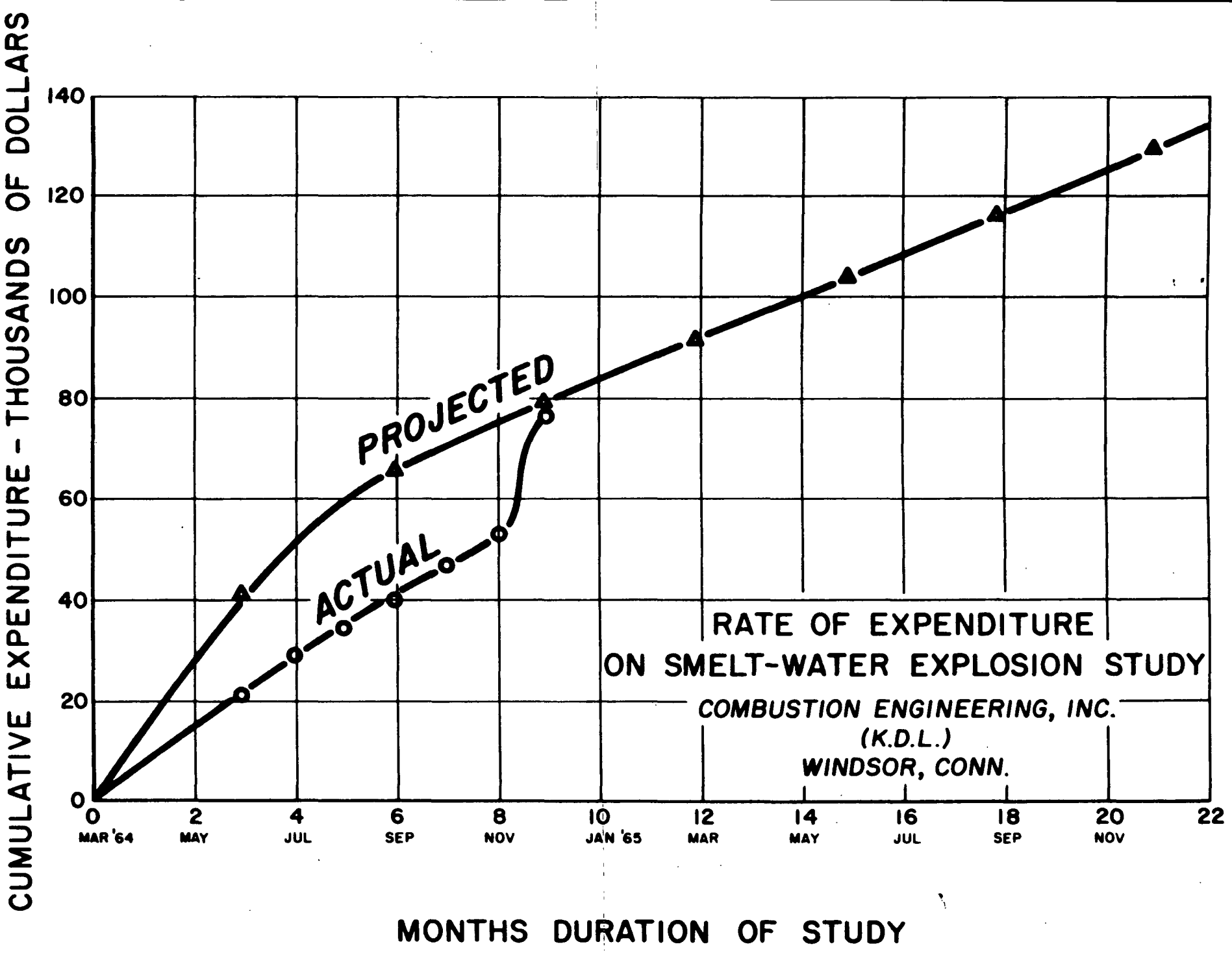
Table 2 (continued)

	ADDITIVE	%	EXPLOSION	SMELT TEMP. (°F) FOR EXPLOSION
95 -	Na_3VO_4	5	Violent	1610
96 -	ZnO	5	Violent	1570
97 -	$Zn_3(PO_4)_2$	5	Mild	1525
98 -	ZrO_2	5	Violent	1700





A THEORETICAL MODEL OF WATER ENCAPSULATION EXPLOSIONS IN MOLTEN KRAFT SMELT


CUMULATIVE EXPENDITURE - THOUSANDS OF DOLLARS
140
120
100
80
60
40
20
0
PROJECTED
ACTUAL
RATE OF EXPENDITURE
ON SMELT-WATER EXPLOSION STUDY
COMBUSTION ENGINEERING, INC.
(K.D.L.)
WINDSOR, CONN.
0 MAR '64
2 MAY
4 JUL
6 SEP
8 NOV
10 JAN '65
12 MAR
14 MAY
16 JUL
18 SEP
20 NOV
22
MONTHS DURATION OF STUDY